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## DETERMINATION OF SULPHATE ACID ESTER IN UNSTABILIZED CELLULOSE NITRATE BY THE HYDROLYSIS METHOD<sup>1</sup>

PAUL E. GAGNON, KARL F. KEIRSTEAD,<sup>2</sup> AND BRIAN T. NEWBOLD<sup>3</sup>

### ABSTRACT

The method of determining sulphate acid ester in unstabilized cellulose nitrates by hydrolysis in acetone/water solution was evaluated. The precision of duplicate determinations for cotton and wood cellulose nitrates containing about 100% sulphate ester was  $-0.1$  to  $+5.9\%$  and  $+0.4$  to  $+9.2\%$ , respectively. With cellulose nitrates containing 69–43% and 69–47% sulphate ester, it was  $+1.8$  to  $+13.4\%$  and  $+0.4$  to  $+21.0\%$ . The sulphate acid ester content of both unstabilized cotton and wood cellulose nitrates increased with decreasing nitrogen content.

### INTRODUCTION

The sulphate acid ester content of cellulose acetate sulphate was estimated by ion exchange methods (5) and more recently by titration in acetone/water solution before and after hydrolysis (2). In a previous paper (3), methods were described for the determination of the sulphate ester content of unstabilized cellulose nitrates.

One of the objects of the present work was to evaluate the hydrolysis method of determining the sulphate acid ester content of unstabilized cotton and wood cellulose nitrates with a view to establishing the reproducibility of the results. The other aim was to determine the relation between the sulphate acid ester content and the nitrogen content of cotton and wood cellulose nitrates.

### EXPERIMENTAL

#### *Cellulose Nitrate*

The nitrations of cotton linters and wood cellulose were performed according to the method mentioned in a recent paper (4) and the sulphate and nitrogen contents were determined by procedures previously described (3, 5).

#### *Hydrolysis of Sulphate Ester Groups in Unstabilized Cellulose Nitrate*

The sulphate acid ester content of cellulose nitrate was determined by the method given in a recent paper (3), except that in the present work the seventh aliquot removed for titration with 0.01 *N* potassium hydroxide was 50 ml. instead of 100 ml.

#### *Zero Hydrolysis of Sulphate Ester Groups in Unstabilized Cellulose Nitrate*

A moist sample (3–4 g.) of the cellulose nitrate was dissolved in 90% acetone/water solution (700 ml.) to prevent hydrolysis and the acidity was determined on aliquots (100 ml.) by titration with 0.01 *N* potassium hydroxide using a Macbeth pH meter.

<sup>1</sup>Manuscript received October 17, 1957.

Contribution from the Department of Chemistry, Laval University, Quebec, Que., with financial assistance from the Defence Research Board of Canada.

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*Evaluation of the pH Meter Titration Method of Determining Acidity*

In a series of experiments, various quantities (5–50 ml.) of 0.1 *N* sulphuric acid were added to 700 ml. samples of acetone/water solution and the acidity was determined on 100 ml. aliquots by titration with 0.01 *N* potassium hydroxide and was measured on a Macbeth pH meter. The average of four determinations on each acetone/water/sulphuric acid aliquot was compared to the theoretical acidity. The mean difference from the theoretical value was  $-4.5\%$ . The standard deviation was 2.8 and the 95% confidence limits were  $-4.5\% \pm 6.3$ , as calculated by the Dean and Dixon method (1).

*Determination of Sulphate Ester in Cellulose Nitrates Prepared by Duplicate Nitrations*

The sulphate acid ester contents of unstabilized cotton and wood cellulose nitrates prepared by duplicate nitrations were determined using the hydrolysis method.

The precision of the ester determinations for cotton cellulose nitrate containing about 100% ester was expressed as follows: the mean difference was 11.0%, the standard deviation 6.0, and the 95% confidence limits were  $11.0\% \pm 8.8$ . For wood cellulose nitrate containing about 100% sulphate ester, the mean difference was 8.0%, the standard deviation 8.7, and the 95% confidence limits were  $8.0\% \pm 12.8$ .

## RESULTS AND DISCUSSION

*Evaluation of the Hydrolysis Method of Determining Sulphate Acid Ester*

In the present work the sulphate acid ester,  $\text{RSO}_4\text{H}$ , contents of a wide range of cotton and wood cellulose nitrates (containing about 7 to 13% nitrogen) were determined by titration in acetone/water solution before and after hydrolysis. Determination of the ester by this method depends on the supposition that hydrolysis of the ester is completed after 24 hours and therefore the 24-hour titer value should give the total sulphate content of the cellulose nitrate. The gravimetric and 24-hour titrimetric sulphates of a series of cotton and wood unstabilized cellulose nitrates are compared in Table I.

TABLE I  
COMPARISON OF GRAVIMETRIC AND TITRIMETRIC SULPHATE PERCENTAGES IN  
CELLULOSE NITRATES

Expt. No.	% $\text{H}_2\text{SO}_4$ in cellulose nitrates			
	Cotton		Wood	
	Gravimetric	Titrimetric	Gravimetric	Titrimetric
1	2.38	2.28	2.36	2.41
2	2.26	2.02	2.17	2.15
3	1.54	1.54	2.13	2.18
4	1.23	1.22	2.12	1.95
5	1.13	1.00	2.02	1.96
6	1.00	0.93	2.01	1.90
7	0.95	0.94	1.34	1.26
8	0.95	0.88	1.33	1.36
9	0.89	0.98	1.30	1.32
10	0.85	0.89	1.23	1.26
11	0.69	0.75	1.04	1.05
12	0.63	0.70	0.93	1.01
13	0.47	0.52	0.91	0.92

There is good agreement between the gravimetric and titrimetric sulphates. The differences are shown statistically in Table II, and the confidence limits for the differences were calculated by the method of Dean and Dixon (1). These results provide evidence

that hydrolysis of the sulphate acid ester was complete after 24 hours. Comparison of 24-hour and 48-hour titrimetric sulphate values, given in Table II, showed that hydrolysis continued slowly, and that the 48-hour titrimetric sulphate was always higher than the gravimetric sulphate, for instance, for cotton cellulose nitrate, about 5%. Therefore the 24-hour titrimetric sulphate was the best indication that hydrolysis of the sulphate acid ester was complete and this value was used for the ester determinations. The precision of 24- and 48-hour titrimetric sulphate determinations on duplicate samples of cellulose nitrates is shown in Table II.

TABLE II  
PRECISION OF TITRIMETRIC TOTAL SULPHATE DETERMINATIONS ON  
CELLULOSE NITRATES

Samples		Difference, %	Standard deviation	95% Confidence limits
Nature	Time, hr.			
Cotton	24*	+0.2	8.2	+0.2 $\pm$ 4.9
Wood	24*	-0.1	4.3	-0.1 $\pm$ 2.6
Cotton	24 and 48	+5.2	2.5	-5.2 $\pm$ 1.5
Wood	24 and 48	+4.8	4.1	-4.8 $\pm$ 2.4
Cotton	24	4.0	1.6	4.0 $\pm$ 1.6
Cotton	48	4.5	1.8	4.5 $\pm$ 1.8
Wood	24	3.2	2.6	3.2 $\pm$ 2.6
Wood	48	4.0	4.2	4.0 $\pm$ 4.2

\*Compared to gravimetric sulphate.

The titration value before hydrolysis of the sulphate acid ester had started was originally determined from a rate of hydrolysis curve by extrapolation to zero time. However, more recently, experiments have been performed with 90% acetone/water solution which effectively stopped hydrolysis of the sulphate acid ester. Determinations of the ester using the zero hydrolysis titer obtained by the latter method have shown that the original zero hydrolysis figure obtained from the rate of hydrolysis curve was always too high. Thus an error of from 8 to 65% for cotton and 7 to 50% for wood cellulose nitrate was introduced into the ester determinations. The error was less when determinations were made on low ester content cellulose nitrates; thus it appears that the rate of hydrolysis when the ester is present in small amount is slower than that when a considerable amount of ester is present. It is evident that the initial hydrolysis of the sulphate acid ester,  $\text{RSO}_4\text{H}$ , is extremely rapid.

The above discussion shows that it is possible to obtain good measures of acidity for samples of cellulose nitrate in which there is no hydrolysis and others in which there is 100% hydrolysis of the sulphate acid ester; therefore the latter can be determined.

It was essential to determine the errors in the method and to establish the reproducibility of the results. The hydrolysis experiments were always performed on duplicate samples and the average results used for sulphate acid ester calculations. The precision of sulphate acid ester determinations on duplicate samples of cotton and wood cellulose nitrates containing about 100% ester is shown in Table III. It is seen that good precision can be obtained. An indication of the experimental error involved in the pH meter titration method for determining the acidity in cellulose nitrate was obtained by means of a series of acidity determinations on sulphuric acid solutions. The 95% confidence limits for the difference between the experimental and theoretical acidity were  $-4.5\% \pm 6.3$ . Therefore in view of the latter error, the precision of the ester determinations mentioned above was

TABLE III  
PRECISION OF SULPHATE ACID ESTER DETERMINATIONS ON DUPLICATE SAMPLES OF  
CELLULOSE NITRATES

Samples		Difference, %	Standard deviation	95% Confidence limits
Nature	Ester, %			
Cotton	100	2.9	3.0	2.9 $\pm$ 3.0
Wood	100	4.8	4.4	4.8 $\pm$ 4.4
Cotton	69-43	7.6	5.8	7.6 $\pm$ 5.8
Wood	69-47	10.7	10.3	10.7 $\pm$ 10.3

good. However, these determinations were made on cellulose nitrates containing close to the maximum amount of sulphate acid ester and therefore the precision obtained was the best possible.

It was expected that the precision of ester determinations would decrease when cellulose nitrates containing less than 70% sulphate acid ester were used. This was the case, as shown in Table III. The precision of ester determinations on cotton cellulose nitrate was better than that for those on wood cellulose nitrate. The precision of sulphate acid ester determinations on very low ester content cellulose nitrates was poor; for instance, for a cotton cellulose nitrate containing 22% sulphate acid ester the difference between duplicate determinations rose to 59%. This fact was not surprising in view of the low sulphate content, 0.47%, of the cellulose nitrate and the fact that the difference in the pH meter titration was -7.4% for the titers obtained.

Several cotton and wood cellulose nitrates were prepared by duplicate nitrations and their sulphate acid ester contents were determined. Typical nitration conditions and ester contents for wood cellulose nitrates are shown in Table IV and the precision of the ester determinations is given in the experimental part. As expected, the precision decreased for both cotton and wood cellulose nitrates.

TABLE IV  
DETERMINATIONS OF SULPHATE ACID ESTER IN WOOD CELLULOSE NITRATES PREPARED BY  
DUPLICATE NITRATIONS

Expt. No.	Temperature, ° C.				Nitrogen, %	Ester, % of total sulphate
	Mixed acid		Drowning water			
	Initial	Maximum	Initial	Maximum		
1	26.0	29.5	25.0	43.0	11.4	81
	23.0	28.0	24.5	56.0	11.4	98
2	23.0	27.1	24.0	43.0	11.7	97
	20.0	23.4	21.0	45.0	11.8	96
3	25.0	29.0	26.0	42.5	10.8	104
	23.0	25.8	24.0	41.0	10.8	97
4	22.0	24.3	21.5	41.5	10.6	94
	20.8	24.1	20.4	40.0	10.7	99

By the hydrolysis method, sulphate acid ester can be determined on duplicate samples of cotton and wood cellulose nitrates containing about 100% sulphate acid ester, with a precision of -0.1 to +5.9% and +0.4 to +9.2%, respectively. When determinations are made on cotton cellulose nitrates containing 69-43% sulphate acid ester, the precision is +1.8 to +13.4%, and for wood cellulose nitrates containing 69-47% sulphate acid ester, +0.4 to +21.0%.

*Relation between Sulphate Acid Ester and Nitrogen Content*

Kullgren (6) using ion exchange studies showed that 12.57% N cellulose nitrate contained about three times as much sulphate acid ester as 13.05% N cellulose nitrate. Miles (7) reported that the proportion of sulphate ester tended to increase with decreasing nitrogen content, and Gagnon *et al.* (3) recently provided some evidence in support of the latter contention.

In the present work, the sulphate acid ester contents of a variety of unstabilized cotton and wood cellulose nitrates were determined and compared to the nitrogen contents of the cellulose nitrates. The results are shown in Fig. 1.

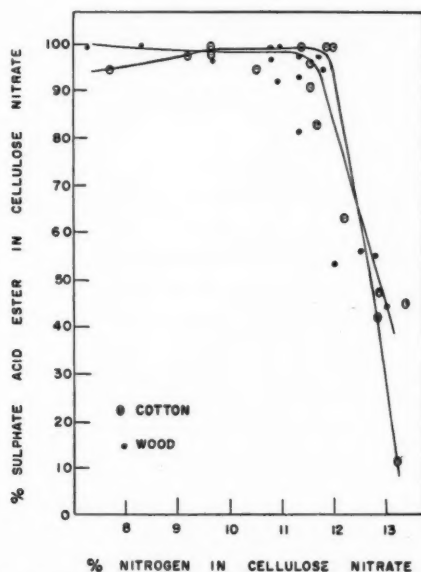


FIG. 1. Relation between sulphate acid ester and nitrogen contents of cellulose nitrate.

It is seen that for cotton cellulose nitrates containing less than 12.2% nitrogen, the sulphate acid ester content is about 100%, but for higher nitrogen contents the sulphate acid ester content rapidly decreases. Similar results were obtained for wood cellulose nitrates.

The sulphate acid ester content of both cotton and wood cellulose nitrate definitely increases with decreasing nitrogen content. This fact is very important evidence for the existence of a sulphate acid ester in unstabilized cellulose nitrate.

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# THE REACTION OF CARBON DISULPHIDE WITH ALUMINA<sup>1</sup>

A. G. PINKUS AND J. S. KIM

## ABSTRACT

The absorption spectrum in aqueous solution of the yellow substance formed by the reaction of carbon disulphide and alumina exhibits absorption maxima at 398 and 325 m $\mu$ . This yellow color is not due to sodium disulphide as previously proposed since the latter substance showed an entirely different spectrum with shoulders at about 360-375 m $\mu$  and 290-300 m $\mu$ . The presence of *both* water and sodium hydroxide in the alumina is necessary for the formation of the yellow color in confirmation of previous work. A study of the gain in weight of the alumina with time of contact with carbon disulphide showed that this reaction begins to level off after about 24 hours. A minimum value for the heat evolved for the alumina - carbon disulphide system was determined as 8.6 cal. per g. of alumina reacting with an excess of carbon disulphide.

## INTRODUCTION

In connection with another problem, spectroscopically pure carbon disulphide was needed. A simple method of purifying many solvents is by passing them through a column of some adsorbent. For example, spectroscopically pure cyclohexane can be obtained by passing it through a column of silica gel (7, 18a) or alumina (19) (after shaking with a nitrating mixture), and peroxides can be removed from ethyl ether, butyl ether, or dioxane by passing through a column containing activated aluminum oxide (4, 18b, c). There are other examples making use of silica gel (18b). When we passed carbon disulphide through a column of activated alumina, it was observed that the entire column turned a yellow color. That this was not due to the removal of impurities from the carbon disulphide was indicated by the fact that passing the same effluent successively through several more alumina columns gave the same result. In view of the widespread use of alumina in chromatography and the use of carbon disulphide as a chromatographic solvent (1, 11) it appeared to be of importance to study this phenomenon. It is stated that the reaction of carbon disulphide with alumina at elevated temperatures produces aluminum sulphide and carbon dioxide (5). At 200° to 500° carbon disulphide reacts with water over activated alumina to produce hydrogen sulphide and carbon dioxide in 98% conversions (2) whereas under milder conditions it is reported that carbonyl sulphide (COS) is formed (16). The formation of a yellow color during the adsorption of carbon disulphide vapors by alumina gel at room temperature was first noted by Perry (15). A thorough study of the action of gaseous carbon disulphide on alumina led to the conclusion on the basis of chemical tests that the yellow color was due to sodium disulphide which was produced by the reaction of carbon disulphide with sodium hydroxide adsorbed on the alumina (13). Since the yellow color was not removed by the usual solvents for sulphur, it was concluded that no free sulphur was present. The reaction products were explained according to the following summarized equations [1]-[6]:



<sup>1</sup>Manuscript received May 3, 1957.

Contribution from the Department of Chemistry, Baylor University, Waco, Texas.



The presence of sodium in the yellow aqueous extract was shown by microchemical tests and in the alumina by spectroscopic means. The presence of sodium hydroxide in the alumina (in equation [5]) was inferred by showing that alumina which had been washed with water (until the aqueous extracts showed the absence of sodium) and reactivated at 400° did not form a yellow color with carbon disulphide. The alumina had been previously saturated with carbon disulphide. In another paper (14) a quantitative study of the same reaction showed that the amount of hydrogen sulphide produced and the intensity of the yellow color qualitatively paralleled the amount of water present, there being an optimum amount (about 8%) below or above which the amount of hydrogen sulphide produced decreased. In our work we made further studies toward a characterization of the reaction of alumina with *liquid* carbon disulphide. We have used absorption spectra to check the conclusion (13) that the yellow color was due to sodium disulphide. Besides various miscellaneous observations, we have made initial studies on the rate by studying the gain in weight of the alumina and also have done some preliminary calorimetric determinations.

#### EXPERIMENTAL

##### *Purification and Preparation of Materials*

ACS grade carbon disulphide was purified by two methods: (a) a previously published procedure (18d, 20) and (b) a simple distillation. No observable differences in results were noted in using these two samples of solvent. Water used in making up solutions was redistilled from potassium permanganate in a nitrogen atmosphere and had a pH of 6.85 to 6.90. Sulphur was purified by recrystallization from redistilled ACS grade carbon disulphide and also by a previously published method (3). No apparent differences in results were detected for these two samples of sulphur. Sodium disulphide was prepared by stirring or shaking ACS analytical grade sodium sulphide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) with the calculated weight of sulphur for about 5 hours and then adding dilute aqueous sodium hydroxide (or distilled water) in small portions with stirring or shaking until all of the solid dissolved. This solution was then diluted up to the desired concentration (approx. 0.0018 *M* for the curve reported). Sodium hydroxide was used in order to repress hydrolysis.

Several commercial grades of alumina were used in this work; however, most of the experiments were done using the same grade in order to have a better basis for comparison. Where a related series of experiments were carried out, samples from the same batch were used. The basic character of the alumina was demonstrated by the following experiments in which the pH of aqueous washings was determined. In a typical determination, a 1.000 g. sample of alumina was stirred with 50 ml. of distilled water (pH 7.00) for 1 hour. The alumina was allowed to settle, the supernatant decanted, and its pH determined by means of a Beckman glass-electrode line-operated pH meter Model H 2. The pH meter was checked at a pH of 7.0 by means of Clark and Lubs buffer mixture (10). Repeated washings with further 50 ml. portions of water showed a rapid decrease in pH from the initial value of 7.42 and then a leveling off to a pH close to 7.0. The data are plotted in Fig. 1. A quantitative estimate of the amount of base in the alumina (calculated as NaOH) was determined by titration of the washings with 0.005 *N* HCl using methyl red indicator. An asymptote was reached at about 11 washings. The total amount of NaOH calculated was 0.40%. The approximate water content of the alumina used in most of the experiments as determined by ignition to constant weight was  $12.6 \pm 0.9\%$  (average of several determinations). A constant weight was attained after about 24 hours of heating.

Dilutions of the yellow reaction product from the alumina - carbon disulphide reaction



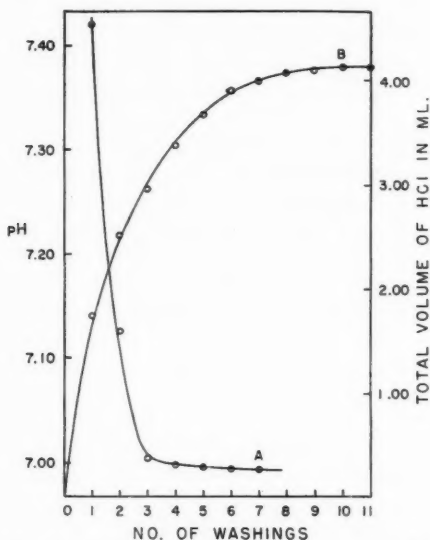


FIG. 1. A, change of pH with number of washings of alumina with water. B, total volume of 0.005 *N* HCl used to titrate washings of alumina with water using 50 ml. of water per washing.

were made by using water saturated with carbon disulphide. Carbon disulphide saturated water was used rather than distilled water alone for two reasons. Since the yellow color was found to disappear when attempts were made to remove the excess carbon disulphide from the alumina *in vacuo*, it was thought that the use of carbon disulphide saturated water would tend to repress this decolorization. Secondly, in order to observe the character of the absorption band at the lower wave lengths, it was found desirable to compensate for the excess carbon disulphide by using the saturated solution of carbon disulphide in the blank absorption cell. The carbon disulphide saturated water was freshly prepared each time just before using. It was found that when distilled water alone was used a more rapid decolorization of the solution occurred.

Various shades of color ranging from yellow to orange were obtained by the reaction of carbon disulphide with the various grades of alumina. Some of the columns themselves showed the same range of colors in different parts of the column. However, the spectra of the aqueous extracts from the various types of alumina showed remarkably similar shapes and absorption band positions. The absorption spectra for the aqueous extract of the yellow reaction product and for sodium disulphide are shown in Fig. 2. In order to show that the use of dilute sodium hydroxide in making up the solutions of sodium disulphide (to repress hydrolysis) did not greatly affect the character of the absorption curve, a curve is also shown for a solution prepared with distilled water alone. (The two are at different concentrations and are not directly comparable as to absorption intensity.)

It was of importance to investigate the possibility that different products might be formed by the reaction of alumina and carbon disulphide depending on the time of contact. In a series of experiments, it was definitely shown that the same absorption spectra were obtained regardless of the time of contact from up to 6 hours down to 1 minute contact before shaking with water and filtering. The amount of the yellow substance produced in general increased with time of contact. In order to check the possibility that the yellow

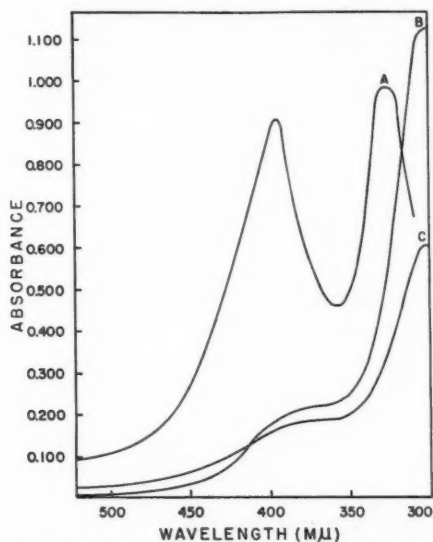


FIG. 2. A, absorption spectrum of aqueous solution of yellow color from the reaction of alumina and  $\text{CS}_2$ . B, absorption spectrum of  $\text{Na}_2\text{S}_2$  in 0.01 *N* NaOH. C, absorption spectrum of  $\text{Na}_2\text{S}_2$  in water.

substance formed from carbon disulphide vapor and alumina (13) might be different than when liquid carbon disulphide was used, we have also run the spectrum of the aqueous extract. The same absorption peaks were obtained.

#### Absorption Spectra

Absorption spectra were determined with a DK-1 Beckman spectrophotometer using matched glass-stoppered 1 cm. quartz cells. A tungsten lamp was the light source for the part of the spectra above  $325\text{ m}\mu$  and a hydrogen lamp below  $375\text{ m}\mu$ . (The overlapping parts of the spectra matched in each case.) A photomultiplier detector was used with both lamps. Absorbance ( $A$ ) was calculated (6, 21) by means of the ratio  $A = \log(I_0/I)$ , where  $I_0$  is the intensity of the incident light and  $I$  the intensity of the transmitted light, both in % transmission. Wavelengths were checked by comparison of accurate values reported (17) for benzene vapor. These were about  $0.1\text{ m}\mu$  higher than the reported values.

#### Calorimetric Studies

The evolution of heat during the passage of carbon disulphide down the column was also noted. It was hoped that a determination of the heat of reaction would aid in the elucidation of the nature of the reaction. A few preliminary calorimetric determinations were made on this reaction following a described method (8). The calorimetric constant was determined by using the reaction of standard solutions of sodium hydroxide and hydrochloric acid. In a typical run, 250 ml. (assumed to be in excess) of carbon disulphide was introduced into the Dewar flask and allowed to come to equilibrium. Then 40.00 g. of alumina was added and the mixture stirred (by using a glass stirrer or a teflon-coated stirring bar) and readings of temperature with time were taken using a Beckman differential thermometer. Since the increase in temperature was not complete even at the end of 18 hours, this indicated a slow approach to equilibrium. Since a more elaborate apparatus would be needed to determine the heat of reaction for such a long reaction period, we

discontinued these experiments at this point. On the basis of the data obtained in the longest experiment, we have calculated (9) a minimum value for the heat of reaction<sup>2</sup> of 8.6 cal./g. of alumina reacting with an excess of carbon disulphide (based on specific heats for alumina and carbon disulphide as deduced from the International Critical Tables).

#### Rate Studies

It was found that on standing the yellow color would disappear from the alumina. This decolorization would also take place when the sample was placed in a desiccator and evacuated using a water pump. This decolorization was shown not to be dependent on the presence of water since it also occurred when the sample was protected during evacuation by means of calcium chloride. Furthermore, it was shown that the alumina gained in weight even though the yellow color had disappeared. This indicated a decomposition of the yellow substance into a gaseous product which was removed leaving a non-volatile colorless product. Since this observation appeared to be an important lead in the elucidation of the nature of the yellow substance, we studied this reaction by determining the gain in weight of the alumina with time during its reaction with carbon disulphide.

In a typical experiment 0.250 g. of alumina was stirred with 25 ml. of carbon disulphide by means of a teflon-enclosed magnetic stirrer, the mixture being kept in a water bath maintained at  $30^{\circ} \pm 1^{\circ}$ . At specified times, the carbon disulphide was decanted and the alumina placed in a desiccator, which was evacuated by means of a water pump. The desiccator was protected from the water pump by means of calcium chloride. The evacuation was carried out until the weight approached a constant value (usually about 24 hours). For the next point, the decanted carbon disulphide was again added to the same alumina and the procedure repeated. The data are plotted in Fig. 3. The yellow color would disappear in about 15 minutes for experiments having a short contact time to about 6 hours for the longer times. The maximum gain in weight of the alumina in our

<sup>2</sup>The referee has suggested that this probably represents a heat of wetting which varies with the activation of the alumina and the amount of water in the carbon disulphide if not anhydrous. Another possibility suggested by the referee is that it may include heat of adsorption, which is often observed with many materials. The referee has kindly furnished the following references dealing with this: J. L. Culbertson and L. L. Winter, *J. Am. Chem. Soc.* **59**, 308 (1937), report a value of 6.7 cal./g. for the heat of wetting of carbon disulphide on silica gel. A. B. Lamb and E. N. Ohl, *J. Am. Chem. Soc.* **57**, 2154 (1935), give values for the heat of adsorption of carbon disulphide on various substances. Bartell in *Coll. Symposium Mon. VII* gives 31 cal./g. for the heat of wetting of carbon disulphide on charcoal and silica gel. We have found a further reference in which heat of wetting values ranging from 2.7 to 4.7 cal./g. adsorbent are listed for various hydrocarbons on alumina: A. S. Russell, W. H. Gitsen, J. W. Newsome, R. W. Ricker, V. M. Stowe, H. C. Stumpf, J. R. Wall, and P. Wallace, *Alumina properties* (Technical Paper No. 10 (Revised), Aluminum Company of America, Pittsburgh, Pa., 1956), p. 42.

The authors feel, however, that the heat of reaction contributes to a large extent to the total heat measured. In support of this, the following points can be made: (a) When carbon disulphide is passed through a column of alumina, sufficient heat is produced to make the column very noticeably warm to the touch. (b) Since we have found no such noticeable heat produced in our experiments with silica gel (see below), we conclude that the heat of wetting produced in this case is insufficient to make the column warm to the touch. (c) Since carbon disulphide dried over phosphorus pentoxide produces this noticeable heat effect, this excludes the possibility of water in the carbon disulphide. (d) Since wetting and adsorption are physical processes it would be expected that the heats of wetting and adsorption would be produced very rapidly. In our experiments we note that heat was still being produced at the end of 18 hours. This would indicate a slow exothermic chemical reaction taking place in addition. (e) Since this point was brought to our attention by the referee, we have conducted the following additional experiment. When alumina was washed free of alkali and reactivated by heating, a heat effect (to the touch) was no longer produced when carbon disulphide was passed through a column of this alumina. (It was also noted that no yellow color was produced.)

In summary we believe that in addition to the heats of wetting and adsorption, the heat of reaction contributed to a large extent to the total heat produced. Actually we have pointed out that our value is a minimum value since the reaction was still incomplete after 18 hours. Furthermore, it is probable that heat was lost during the time of measurement since our apparatus was not designed for a long period of measurement, as we have pointed out. It should be possible to obtain an estimate for the heat of reaction by measuring the heat of wetting (and adsorption) for alumina washed free of alkali and dried and subtracting this value from the total heat obtained for the alumina before washing. (This assumes that the heats of wetting and adsorption are nearly the same for the two alumina samples.) Since we do not have the equipment necessary to obtain the latter data accurately, however, we are not planning any further work along these lines. We thank the referee for bringing these points to our attention.

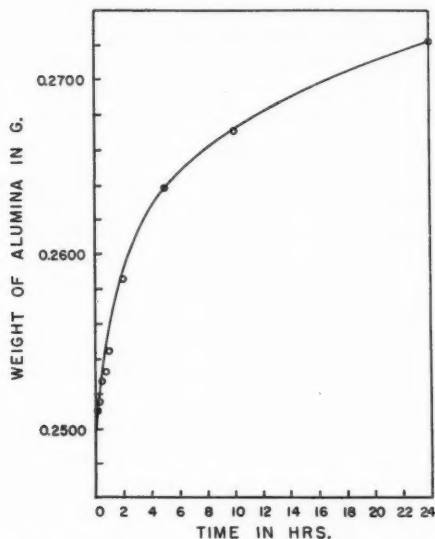


FIG. 3. Gain in weight of alumina on stirring with  $\text{CS}_2$  for varying amounts of time using the same  $\text{CS}_2$  each time.

experiments was 0.0045 g./0.2500 g. of alumina or 0.1800 g./10 g. of alumina. The saturation value reported by Perry (15) for the *adsorption* of carbon disulphide on alumina gel was 2.96 g./10 g. of alumina. It should be pointed out that in his work he was measuring the increase due to the yellow reaction product plus *adsorbed* carbon disulphide whereas in our work we are measuring mainly the *colorless reaction product*.

#### Miscellaneous Experiments and Observations

(a) When alumina which had been washed with water and dried was shaken with carbon disulphide, no yellow color was formed. This result confirms the previous observations (13). However, after a longer period of contact, the alumina turned a light brown color. This color, however, was not soluble in water, in contrast to the previously mentioned yellow substance, and thus appears to be a different substance. (b) When alumina (previously ignited to constant weight) was treated with dry carbon disulphide, no color formed even after they had been in contact for 1 week. This is in accord with the findings of Munro and McCubbin (14), who found that the catalytic activity of their alumina gel decreased to zero at zero water content of the gel. (c) The odor of hydrogen sulphide was quite evident from the reaction of alumina and carbon disulphide in agreement with the previous observations (13). (d) Silica gel did not form a yellow color with carbon disulphide, and no noticeable heat effect (to the touch) was noted when carbon disulphide was passed through a column of silica gel.

#### RESULTS AND DISCUSSION

The absorption spectrum for the yellow product of the reaction between alumina and carbon disulphide is shown in Fig. 2 and shows two maxima at 398 and 325  $\text{m}\mu$ . The curves for sodium disulphide (shown in the same figure) show two shoulders: 360–375  $\text{m}\mu$  and 290–300  $\text{m}\mu$ . To our knowledge the absorption spectrum of sodium disulphide below 400

$m\mu$  has not been previously reported. Recently the curves for potassium disulphide and other polysulphides were reported (12) *above* 400  $m\mu$ . However no structure is evident in this region. It is interesting that hydrolysis causes only minor differences in the spectra of the two. We have also noted that the shoulders broaden with dilution for both the basic and water solutions. For example, when the basic solution was diluted to about 0.0006 *M* the shoulder extended from about 360 to 380  $m\mu$ . In either case it is evident that these spectra differ markedly from the spectrum of the yellow reaction product from alumina and carbon disulphide. In deference to Munro and McCubbin, it should be pointed out that absorption spectra were not generally available at that time. Evidently the yellow substance must respond to the same chemical tests as sodium disulphide. This observation may be helpful in the elucidation of the nature of this substance.

It is clear from our results and those of Munro and McCubbin that *both* water and sodium hydroxide must be necessarily present in the alumina for the formation of the yellow color. Any mechanism to explain the formation of the yellow color must take these facts into account.

The studies on the gain in weight of the alumina show that equilibrium is approached after more than 24 hours of reaction. This indicates the approximate amount of time needed for a calorimetric study.

We are continuing a study of other possible compounds as the cause of the yellow color in question.

#### ACKNOWLEDGMENTS

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## BLOCK AND GRAFT POLYMERS

### I. GRAFT POLYMERS FROM ACRYLAMIDE AND ACRYLONITRILE<sup>1</sup>

M. L. MILLER

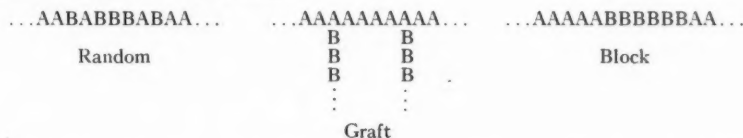
#### ABSTRACT

Graft polymers of acrylonitrile and acrylamide with from 1 to 20 grafts have been prepared by chain transfer to polymer and by photolysis of a copolymer containing a few per cent of  $\alpha$ -chloroacrylonitrile. The intrinsic viscosities and softening points have been measured and the dependence of these properties on the number of grafts observed.

#### I. INTRODUCTION

The properties of homopolymers and, to an even greater extent, those of copolymers can be changed by changing the arrangement of the monomer units in the polymer molecule. This opens up the possibility of preparing polymers with new and improved properties from old monomers and old combinations of monomers.

There are at least three ways in which monomer units A and B can be arranged in a copolymer. These three types of copolymers, random, graft, and block, are illustrated by the schematic diagrams shown below.



It was the object of this series of investigations to prepare block and graft polymers with known lengths and numbers of blocks and grafts and to use these polymers to study the effect of different arrangements of monomer units on some representative physical properties. The monomer pairs chosen for this work were acrylonitrile and acrylamide and acrylic acid and acrylamide. The work falls into two parts, the preparation of the polymers and the study of their properties. This paper describes the preparation and study of graft polymers. The following paper will treat block polymers.

#### II. EXPERIMENTAL PREPARATION OF GRAFT POLYMERS

Two methods were used to prepare graft copolymers. These methods were: (1) chain transfer to polymer, and (2) photolysis of polymers containing a small amount of copolymerized  $\alpha$ -chloroacrylonitrile.

##### *Preparation of Graft Copolymers by Chain Transfer to Polymer*

In the preparation of graft copolymers by chain transfer, the backbone polymer was dissolved in 65–70% sodium perchlorate, the second monomer added, and the grafting carried out at 55° C. with a persulphate–bisulphite catalyst. Either polyacrylonitrile or polyacrylamide could be used as the backbone polymer.

Sodium perchlorate solution was used as a solvent because it dissolves the graft copolymer and both homopolymers. Furthermore, this solvent is not a chain transfer medium

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Contribution from the Stamford Laboratories, Research Division, American Cyanamid Company, Stamford, Connecticut. Presented in part before the Seventh Canadian High Polymer Forum, Sarnia, Ontario, Canada, November 8–9, 1956.



and it does not compete with the grafting reaction. A further advantage is the fact that sodium perchlorate, unlike other possible solvent salts, is not attacked by the oxidizing agent in the catalyst.

A typical preparation was as follows: 999 g. of  $\text{NaClO}_4$  was dissolved in 560 g. of oxygen-free water. Eleven grams of polyacrylonitrile (molecular weight 175,000) and 33 g. of acrylamide were dissolved in this solution and the polymerization carried out at  $55^\circ\text{C}$ . under a blanket of  $\text{CO}_2$  for 4 hours. 0.28 mole of ammonium persulphate and 0.07 mole of sodium metabisulphite were used as catalyst. The yield was: 20.5 g. graft polymer (containing 50 mole % acrylonitrile and 50 mole % acrylamide), 6 g. of polyacrylamide (recovered from water-solubles after dialysis to remove salts), and no dimethylformamide-soluble polymer.

By this method, polymers with as much as 50 mole per cent of the grafted monomer and with from 1 to 6.5 grafts per molecule were obtained. This method suffered from the disadvantage that excessive amounts of catalyst were required. Nevertheless, a supplementary experiment showed that the backbone polymer, when treated as in a grafting experiment but in the absence of a second monomer, suffered little or no reduction in intrinsic viscosity.

#### *Photolysis of Copolymers of Alpha-Chloroacrylonitrile*

The second and preferred method for making graft copolymers was a modification of the method used by M. H. Jones and associates (6, 7, 8). These workers brominated polystyrene to the extent of a few per cent and then photolyzed the partly brominated polystyrene in the presence of methyl methacrylate to make a graft copolymer. In our experiments, we have used for backbone polyacrylonitrile or polyacrylamide which has been copolymerized with one to three mole per cent of alpha-chloroacrylonitrile. Alpha-chloroacrylonitrile is convenient for this purpose because the copolymer containing 1-3% chloroacrylonitrile is stable to storage under ordinary laboratory conditions and to solution in and precipitation from such solvents as concentrated salt solutions and ethylene carbonate. It is less stable in dimethylformamide, but can be handled in this solvent if neutral and if the temperature is kept low. In spite of the relative stability, the presence of the nitrile on the same carbon as the chlorine acts somewhat like a second halogen and sensitizes the copolymer to photolysis (9).

The copolymers of  $\alpha$ -chloroacrylonitrile and acrylonitrile were prepared by the following recipe:

- 76 cc. redistilled methanol
- 242 cc. oxygen-free water
- 5.75 cc. catalyst A (17.3 g. ammonium persulphate in 240 cc. water)
- 2.55 cc. catalyst B (7.68 g. sodium metabisulphite in 240 cc. water)
- 1.60 cc. catalyst C (0.45 g.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 100 cc. water)
- 30 cc. acrylonitrile
- 1.25 cc.  $\alpha$ -chloroacrylonitrile (b.p.  $87.5\text{--}88^\circ\text{C}$ . uncorr.,  $n_D^{25} = 1.4257$ )
- 200 mg. sodium lauryl sulphate

The mixture was cooled to  $-10^\circ$  to  $-14^\circ\text{C}$ . before monomer or catalyst was added. The mixture was kept at  $-10^\circ$  to  $-14^\circ\text{C}$ . under a blanket of  $\text{CO}_2$  for 120 hours. Yield 100%, molecular weight about 50,000.

In a grafting experiment, the polymer containing  $\alpha$ -chloroacrylonitrile was dissolved in 66-70% sodium perchlorate or 50%  $\text{NaSCN}$ , the second monomer added, and the solution photolyzed for 2-4 hours at  $25^\circ$  to  $35^\circ\text{C}$ . in a quartz tube under a G.E. Sun Lamp.



An illustrative experiment used:

0.50 g. polyacrylonitrile (molecular weight 200,000, 1.5%  $\alpha$ -chloroacrylonitrile)

50 g. of 70% NaClO<sub>4</sub> solution

2 g. acrylamide

Yield: 0.3 g. graft polymer (40 mole % acrylonitrile, 60 mole % acrylamide)

0.0 g. polyacrylonitrile

0.023 g. polyacrylamide (molecular weight 84,000)

#### *Isolation and Characterization of Graft Polymers*

After the grafting reaction was completed, the reaction mixture, whether prepared by the first or second procedure, was poured into methanol. The precipitate was extracted alternately and repeatedly with hot water and hot dimethylformamide.

Three or four extractions with each solvent were required. In each extraction, the polymer was intimately dispersed in the extracting medium. During this extraction, some polymer stuck to the glassware or was decanted with solvent. These losses resulted in a lowered over-all recovery of backbone polymer.

The graft polymer was insoluble in both dimethylformamide and water. The dimethylformamide extract contained any free polyacrylonitrile that was present. This extract was concentrated and methanol added to precipitate the polymer. The water extract contained any free polyacrylamide that was present. The water extract was concentrated, dialyzed to remove salt, and freeze-dried. In general, none of the backbone polymer was recovered ungrafted, but there was usually a relatively large amount of the homopolymer of the composition used to make the grafts. The composition of all polymers was determined by infrared examination of thin films. Films of copolymers were cast from dimethylsulphoxide and those of homopolymers from water or dimethylformamide. After evaporation of the solvent, the films were washed three times in boiling methanol and dried 16 hours at 117° C. under vacuum. A preliminary experiment showed that this treatment reduced the solvent content to less than  $\frac{1}{2}$ %.

Because the object was to prepare graft polymers with well-defined structures, the initial backbone polymers had to be unbranched. For this reason, backbone polymers were prepared by polymerization at 0° C. Since polyacrylonitrile (11) and polyacrylamide (4) have very little branching when prepared at 50° C., polymers prepared at zero degrees can be considered essentially unbranched.

Fractions of these unbranched polymers were used as backbones. Fractions of polyacrylonitrile were prepared by precipitation from dimethylformamide by a mixture of ether and heptane (5) and fractions of polyacrylamide were prepared by precipitation from water by dioxane.

The molecular weight of polyacrylonitrile was estimated from intrinsic viscosity measured in dimethylformamide at 30° C. and calibrated against light scattering data (2, 11). The molecular weight of polyacrylamide was estimated from intrinsic viscosity measured in water at 30° C. and calibrated against molecular weights obtained by light scattering (1) and by sedimentation (13).

The chlorine-containing polymer was sensitive to degradation when attempts were made to fractionate it by the methods used with polyacrylonitrile. Therefore, it was dissolved, at 0° C., in neutral dimethylformamide to give a 1.0% solution. An equal volume of 40% ethanol was added and the clear solution fractionated by spinning in a preparative ultracentrifuge with an iced rotor at 78,000g.

The graft polymers, although insoluble in water and dimethylformamide, dissolved

readily in dimethylsulphoxide and in concentrated salt solutions. This showed that they were not cross-linked. The polymers gave optically clear films and optically clear concentrated solutions that did not show a two-phase structure when examined visually or by phase contrast microscopy. These facts are evidence that the polymers are graft polymers and not mixtures of homopolymers.

Since none of the backbone polymer was recovered ungrafted, it is evident that all of the polymer initially present has been incorporated in the graft polymer. Therefore, the molecular weight of the backbone in the graft polymer is the same as that of the dead polymer used. On this basis, the molecular weight of the graft polymer was computed from the molecular weight of the backbone polymer and the composition of the graft polymer. If we make the assumption that the molecular weight of the chains that did not become attached is the same as that of the chains that grafted on, then we can calculate the average number of grafts on the backbone chain. This assumption is reasonable and is supported by experiment (8, 10). The graft polymers shown in Table I have been characterized in this way.

TABLE I  
SUMMARY OF GRAFT COPOLYMERS

Backbone polymer	Mole % acrylonitrile in graft polymer	Molecular weight of:		Number of branches	Softening point, °C.
		Graft polymer	Branches		
Polyacrylamide	15-20	185,000	3,800	6.7	162
Polyacrylamide	20	145,000	15-25,000	1-1.5	210
Polyacrylonitrile	25	1,000,000	38,000	21	145
Polyacrylonitrile	40	600,000	84,000	4.8	162
Polyacrylonitrile	50	420,000	38,000	6.3	180
Polyacrylonitrile	50	180,000	38,000	2.7	200
Polyacrylamide	80	640,000	465,000*	1	172

\*Does not check with composition.

### III. PROPERTIES OF GRAFT POLYMERS

#### *Intrinsic Viscosity*

Intrinsic viscosities were measured in 50% (by weight) aqueous sodium thiocyanate solution at 30° C. This is a solvent for graft copolymers and both homopolymers. Ostwald viscometers with flow times for the blank from 67.5 to 289.4 seconds were used. A kinetic energy correction was applied. Tests for the viscosity slope constant  $k'$  (3) were run on the graft polymers that had 2.7 and 6.3 grafts per molecule. Solutions were made up by weight and diluted by weight and the charge was weighed into the viscometer. There was no evidence for a dependence of  $k'$  on the number of grafts.

For graft polymers, linear random copolymers, and for polyacrylonitrile  $k'$  was  $0.34 \pm 0.02$ .

Table II summarizes the viscosity data. This table lists the intrinsic viscosity of the backbone polymer, of the graft polymer, and the intrinsic viscosity calculated for a hypothetical mixture of homopolymers each having the same molecular weight as the graft polymer. It will be noted that in every preparation the intrinsic viscosity of the graft polymer is greater than that of the backbone polymer. This must be true if the preparation has been carried out correctly.

In all but the first sample, the intrinsic viscosity of the graft polymer is less than that calculated for an ideal mixture of homopolymers of the same molecular weight. This is to

TABLE II  
INTRINSIC VISCOSITY OF GRAFT POLYMERS IN 50% SODIUM  
THIOCYANATE AT 30° C.

Number of branches	Intrinsic viscosity, dl./g.		
	Backbone	Graft polymer	
		Observed	Observed/computed
1	1.35	5.1	1.13
1-1.5	1.10	1.30	0.95
2.7	0.85	1.50	0.63
4.8	2.10	4.3	0.63
6.3	2.00	3.3	0.73
6.7	1.00	1.60	0.68
21	2.10	5.6	0.58

be expected because of the branched structure. It is also to be expected that, as the number of grafts increases, the ratio of observed to computed viscosity will decrease. The last column in the table shows that this is only roughly true.

#### Softening Points

Softening points were measured as sticking points using a calibrated Parr melting point bar in an atmosphere of dry nitrogen. They were reproducible to  $\pm 7^\circ$  C. The tests were made on films 5 to 10 mils thick that were cast from dimethylsulphoxide. After being dried in a forced draft oven at  $110^\circ$  C., the films were washed in boiling methanol and in boiling acetone and dried in vacuum at  $117^\circ$  C. for 16 hours. After this treatment, the films retained less than  $\frac{1}{2}\%$  of solvent. The films were boiled in acetone and vacuum dried another 16 hours before testing. The observed softening points are shown in Table I. Fig. 1 plots the difference between the observed softening points and a line joining the

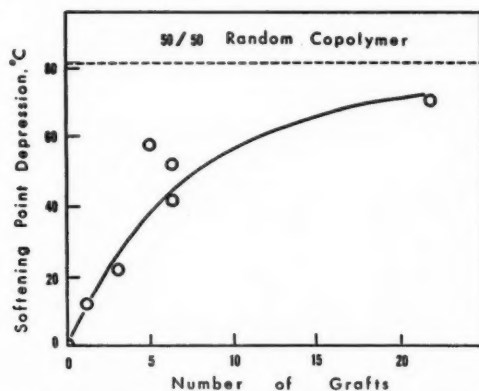


FIG. 1. Dependence of softening point depression on number of grafts.

softening points of the two homopolymers (12) against the number of grafts. Polymer 4 (Table I), for which the number of grafts is subject to some doubt, has been omitted from the figure. As the number of grafts increases, the softening point decreases and approaches, as a limit, the softening point of the 50/50 random copolymer.

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## BLOCK AND GRAFT POLYMERS

### II. BLOCK POLYMERS FROM ACRYLAMIDE AND ACRYLONITRILE AND ACRYLAMIDE AND ACRYLIC ACID<sup>1</sup>

M. L. MILLER

#### ABSTRACT

Block polymers of acrylamide and acrylonitrile and of acrylamide and acrylic acid have been prepared by photolysis of polymers with end groups that contained bromine. The intrinsic viscosities and softening points of these polymers have been measured and compared with the viscosities and softening points of random copolymers having the same composition and molecular weight.

#### I. INTRODUCTION

The preceding paper describes the preparation and study of graft polymers of acrylamide and acrylonitrile. This paper is concerned with block polymers of acrylamide-acrylonitrile and acrylamide-acrylic acid.

#### II. PREPARATION OF POLYMERS

##### *Development of Method*

Block polymers were made by a modification of the method devised by Dunn, Stead, and Melville (2). This method uses a polymer with end groups containing bromine to sensitize the photopolymerization of a second monomer. Conditions necessary to make the initial blocks of polyacrylonitrile and the block polymer were worked out on the basis of the following preliminary experiment.

In this experiment, acrylonitrile and mixtures containing equal volumes of acrylonitrile and bromoform or dibromomethane or monobromoethane were sealed in Pyrex tubes. These tubes were partly immersed in ice water and exposed to the light from a G.E. sun lamp, screened by 5 mm. of window glass for 3 hours. The glass was removed and irradiation continued for 3 hours more. The results, shown in Table I, indicate that one bromine

TABLE I  
TIME REQUIRED TO POLYMERIZE ACRYLONITRILE WITH DIFFERENT  
PHOTOSENSITIZERS, HOURS

Additive	Light screened*		Light unscreened†	
	Trace	Thick polymer	Trace	Thick polymer
CHBr <sub>3</sub>	1	2¾	—	—
CH <sub>2</sub> Br <sub>2</sub>	>3	Long	½	2¾
C <sub>2</sub> H <sub>5</sub> Br	>3	Long	2	>3
None	>3	Long	2	>3

\*Cutoff 310 mμ.

†Cutoff 290 mμ.

atom is split off from the bromoform with the glass screen in place, but not from the compounds containing only one or two bromine atoms on a single carbon. With the glass removed, bromine is split off from a carbon loaded with two bromines after ½ hour exposure. A bromine atom on a carbon loaded with a single bromine is not touched before

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the blank, containing acrylonitrile alone, starts to polymerize. These are the conditions needed to prepare block polymers.

*Preparation of Block Polymers from Acrylonitrile and Acrylamide*

The initial blocks of polyacrylonitrile were made as follows. Acrylonitrile and bromoform were mixed in the proportions 25 cc. acrylonitrile to 15 cc. of bromoform. The mixture was sealed in 12 mm. i.d. Pyrex tubes containing approximately 10 cc. each. The tubes were placed in an ice bath with 5 mm. of ordinary window glass  $2\frac{1}{2}$  inches above them and a G.E. sun lamp  $3\frac{1}{2}$  inches above the glass. The tubes were irradiated in 15-minute exposures (with cooling and mixing between exposures) for a total of 3 hours' exposure. The tubes were opened and the contents poured into methanol. The polymer was washed with methanol three times, then with acetone, and air dried. The molecular weight was estimated from the intrinsic viscosity in dimethylformamide at 30° C. (1, 3). Two preparations by this method had molecular weights of 135,000 and 265,000.

A typical recipe for adding the polyacrylamide block was as follows. Two grams of the polyacrylonitrile (prepared as above) was dissolved in 235 cc. of 50% (by weight) sodium thiocyanate solution (prepared and kept free from oxygen by flushing and blanketing with CO<sub>2</sub>). Three grams of acrylamide was added and the solution sealed in Pyrex tubes and exposed to the light from an unscreened sun lamp at 30–50° C. The product was worked up as described for graft polymers (4). Even though the ratio of acrylamide to polyacrylonitrile was varied within relatively wide limits, 2/1, 2/3, 2/5, 2/6, the product always had about the same composition as determined by infrared, i.e., 60 mole per cent nitrile and 40% amide. This is due, apparently, to the fact that the same solvent treatment was used for isolating the product. In one experiment, a small amount of a second block polymer containing 35 mole per cent nitrile and 65 mole per cent amide was isolated as a less soluble portion of the water solubles. Less than a third as much of this was obtained as of the main product. Little or none of the initial polyacrylonitrile block was recovered.

*Preparation of Block Polymers from Acrylic Acid and Acrylamide*

Blocks of polyacrylic acid were made by essentially the same method as was used for making blocks of polyacrylonitrile. Mixtures of acrylic acid and bromoform (in some experiments diluted with benzene) were irradiated as above but for only  $\frac{2}{3}$  to  $1\frac{1}{2}$  hours. The contents of the tubes became solid but were entirely soluble in water. After irradiation was finished the tubes were opened and the contents washed into benzene, centrifuged, and rewashed with benzene several times to remove bromoform and monomer. The polymer was dissolved in water and freeze-dried. Its molecular weight was estimated from the intrinsic viscosity measured in dioxane (5). This procedure gave polymers with molecular weights ranging from 145,000 to 540,000.

The polyacrylamide block was added to this polyacrylic acid block by the method previously used to add acrylamide to polyacrylonitrile. In an illustrative preparation, approximately  $\frac{2}{3}$  of a gram of the undried or freeze-dried polyacrylic acid with end groups which contained bromine was dissolved in 100 cc. of oxygen-free water under a blanket of carbon dioxide. Two grams of acrylamide was added and the solution was sealed in tubes and irradiated by an unscreened sun lamp. Irradiation was carried out at 25° to 35° C. for 2 hours. The contents of the tubes were poured into 500 cc. of dioxane and extracted twice with hot dioxane. The flow sheet, Fig. 1, shows the work-up of the product. The over-all recovery of initial polyacid was about 40% and the ungrafted acid was 25% of the starting polyacid block.



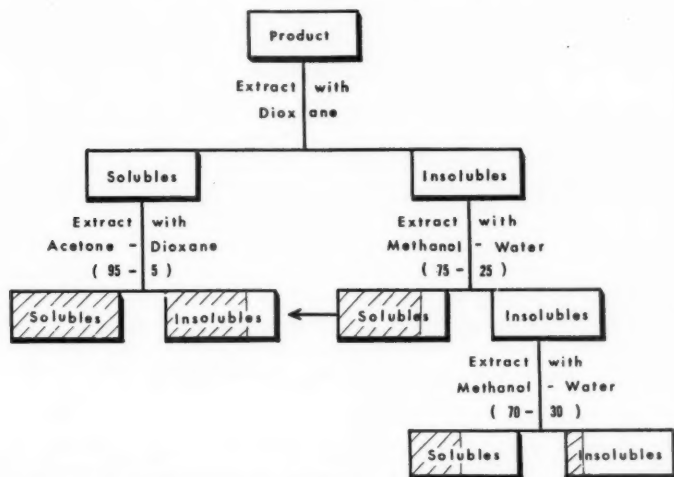
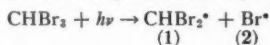


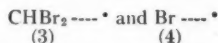
FIG. 1. Separation of block polymers of acrylic acid and acrylamide from reaction mixture. Shaded areas represent per cent of fraction that is acrylic acid.

#### Discussion of Preparation

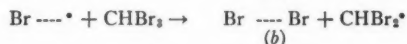
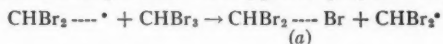
In the first step, irradiation caused the photodecomposition of the bromoform,



Each of these radicals, (1) and (2), can initiate polymerization to give polymeric radicals (3) and (4):



These four types of radicals can terminate by combination with one another, by disproportionation, or by chain transfer to solvent or to monomer. Although initially there are approximately equal numbers of moles of acrylonitrile and bromoform, the amount of acrylonitrile decreases very rapidly as polymerization proceeds. Thus, it is reasonable to assume that, for the bulk of the reaction, termination is by chain transfer to solvent. This mode of termination would produce two types of polymer molecules (a) and (b), i.e.,



This process would also result in the liberation of a free radical which could, in turn, initiate other chains so that the reaction could, and probably does, become autocatalytic. Molecules of type (b) will be unaffected by further irradiation and will be isolated as unchanged polyacrylonitrile in the work-up of the product. Molecules of type (a), when photolyzed, will add on acrylamide to form block polymer. These polyradicals could terminate by (1) combination with one another, (2) combination with  $\text{Br}^\bullet$ , or (3) disproportionation. Except where termination is by combination of radicals, all block polymers will consist of two blocks:





Here X is either Br or double bond. If there is a significant amount of combination of radicals of type (b) with one another, there will be polymer molecules made up of three blocks. More complex molecules are possible, but they are less probable.

### III. RESULTS

#### *Block Polymers Containing Acrylonitrile and Acrylamide*

Table II summarizes the block polymers of acrylonitrile and acrylamide that have been prepared. Column 1 gives the mole per cent of nitrile, measured by infrared; column 2 the molecular weight of the block polymer as computed from the molecular weight of the initial block and the composition of the polymer; columns 3 and 4 give the intrinsic viscosity in 50% sodium thiocyanate as measured and as computed for a hypothetical mixture of homopolymers each having the same total molecular weight as the block polymer. It is seen that, except in one instance where the molecular weight is very high, the computed viscosity is in good agreement with the observed.

TABLE II  
BLOCK POLYMERS FROM ACRYLONITRILE AND ACRYLAMIDE

Mole % of acrylonitrile	Molecular weight $\times 10^{-3}$	Intrinsic viscosity in 50% NaSCN at 30° C., dl./g.	
		Observed	Computed
66	196	—	—
63	360	—	—
60	257	2.15	2.19
62	250	2.25	2.22
60	500	—	—
35	935	—	—
60-65	478	3.34	3.45
70-80	276	2.75	2.71
50	620	5.2	4.0

#### *Block Polymers Containing Acrylic Acid and Acrylamide*

Table III describes two block polymers of acrylamide and acrylic acid. The molecular weight of these polymers was estimated in two ways, both of which are approximations.

In the first method the polymers were hydrolyzed until the hydrolysis stopped. The viscosity of this hydrolysis product was measured in 1 N NaOH and the corresponding molecular weights read from a plot of molecular weight vs. viscosity for random copolymers of the same acid contents.

TABLE III  
INTRINSIC VISCOSITIES OF BLOCK POLYMERS FROM ACRYLIC ACID AND ACRYLAMIDE

Fraction No.	Acid	Molecular weight ( $\times 10^{-3}$ ) by:		Intrinsic viscosity, dl./g.		
		Hydrolysis	Computation	Observed	Computed	Of random polymer
2	75	310	366	1.60	1.55	2.30
3	45	637	610	2.50	2.45	3.80

In the second method the molecular weight was computed from the composition of the copolymer on the assumption that the initial block of acrylic acid has not been fractionated by the processing of the mixture containing the graft polymer. The agreement of the molecular weights by the two methods is good. Columns 3 and 4 in Table III compare

the intrinsic viscosities measured in 1 *N* sodium nitrate, after neutralization, and the intrinsic viscosities computed for a hypothetical mixture of homopolymers each having the same molecular weight as the block polymer. The agreement between the observed and computed values is good.

This agreement between observed and computed viscosities for block polymers (with two or three blocks) is to be contrasted with the intrinsic viscosity of linear random copolymers. In general it is not possible to estimate the intrinsic viscosity of a linear random copolymer from measurements of the viscosity of homopolymers made from the two comonomers that were used to prepare the random polymer.

This unpredictability is illustrated by the data in column 7 of Table III which gives the intrinsic viscosity of linear random copolymers of acrylic acid and acrylamide that have the same composition and molecular weight as the block polymers. These viscosities are far greater than the computed viscosities or the viscosities of the block copolymers.

#### IV. PROPERTIES OF BLOCK POLYMERS

##### *General*

The properties of random copolymers from two monomers usually pass through a maximum or a minimum as the composition is changed from 100% of one comonomer to 100% of the other. If, however, the copolymer contains one long graft or, better yet, two or three long blocks the value of a given property should be very close to the value computed for a hypothetical mixture of two homopolymers each having a molecular weight equal to that of the block polymer as a whole. Preceding measurements have shown that this is true for intrinsic viscosity. It is of interest to examine the validity of this mixture rule for block copolymers with some other properties. This has been done for softening points of acrylonitrile-acrylamide copolymers and for acid dissociation constants for acrylic acid-acrylamide copolymers. The work on dissociation constants will form the subject of the third paper in this series.

##### *Softening Points*

Softening points of the copolymers of acrylamide and acrylonitrile were measured as

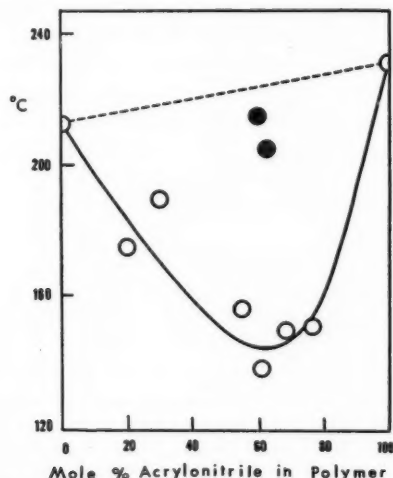


FIG. 2. Softening point of random and block copolymers of acrylamide and acrylonitrile; ○—random copolymers, ●—block copolymers.

sticking points of films using a calibrated Parr melting point bar in an atmosphere of dry nitrogen. The measurements were reproducible to  $\pm 7^\circ \text{C}$ . They are to be regarded as empirical values useful for comparison. The tests were made on films 5 to 10 mils thick that were cast from dimethylsulphoxide. After being dried in a forced draft oven at  $110^\circ \text{C}$ ., the films were washed in boiling methanol and in boiling acetone and vacuum dried at  $117^\circ \text{C}$ . for 16 hours. After repetition of this treatment, the films retained less than  $\frac{1}{4}\%$  of solvent. Fig. 2 plots the softening point of random copolymers of acrylonitrile and acrylamide against mole per cent of acrylonitrile. Open circles designate random copolymers and filled circles block polymers. It is seen that the softening point of random copolymers falls off very sharply as the composition is changed from 100% of one comonomer to 100% of the other. For block polymers, the softening points are very close to a line joining the softening points of the two homopolymers.

#### CONCLUSIONS

These experiments have shown that the softening points and intrinsic viscosities of block polymers having two or three long blocks can be computed from the corresponding properties of the homopolymers. This can be done also as a first approximation for graft polymers with only one graft (4). As the number of grafts increases, the deviations from the expected values become greater as a result of the branched structure and the increased heterogeneity.

#### ACKNOWLEDGMENTS

It is a pleasure to thank Miss C. A. Ederle, Mr. R. M. McGrath, and Mr. R. Polistina for assistance with the experimental work and Miss E. C. Eberling for the infrared analyses.

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## A MODIFICATION OF THE DIRECT CURRENT CONDUCTANCE METHOD<sup>1</sup>

G. D. GRAHAM AND O. MAASS

### ABSTRACT

A modification in the employment of the direct current method of measuring conductivities is described. The main objective is that pure metallic probe and current carrying electrodes can be used, thus making it possible to investigate the conductivity of solutions such as hydrogen peroxide, aqua regia, etc. This necessitates a choice of electrodes which are inert to such solutions. An electrometer having an infinite resistance so as to avoid any polarization at the probes, in this case the quadrant electrometer, is described in its use as a null instrument. An accuracy as high as or greater than that of the alternating current method could be obtained. Furthermore, this method entails greater equipment economy and simplicity in apparatus required.

### INTRODUCTION

In the measurement of electrolytic conductivity in water and other solvents, two main methods have been used, the alternating current method, the more common one, in which polarization is compensated for depending on frequency, capacity, and inductance, and the direct current method in which the so-called probe electrodes (as will be explained later on) bring in experimental hazards. It has been shown by Gordon (5) and co-workers that the direct current method with the experimental setup he devised will give the same accuracy in measurements that the alternating current method gives. Previous to Gordon, a number of other workers (1, 2, 3, 8) had used the direct current method, and since Gordon's publication others have substantiated his find, among them Schiff (4), Lim (7), and Ives (6).

In planning a number of investigations of electrolytic conductivity of certain systems, hydrogen peroxide solutions, so-called aqua regia solutions, and in general to make use of the direct current method, it was thought that it would be desirable to have pure metallic probe electrodes and current carrying electrodes all made of the same pure metal. For hydrogen peroxide solutions, electrodes of pure tin, which does not cause any decomposition of hydrogen peroxide, are the best to use. For aqua regia, tungsten electrodes are the best and also for every purpose in which conductivities are measured; the nature of the material of the electrodes would not diminish the accuracy of the results obtained by using the direct current method. Furthermore, the direct current method, as used by others and with certain simplifications described below, makes it possible to determine accurate conductivity data over the range of conductivities from pure solvents to highly conducting solutions without the financial expenditures for instrumentation involved in the alternating current method.

### EXPERIMENTAL

As indicated above, in the direct current method, polarization of the probe electrodes has to be minimized. In this, a great deal depends on the nature of the instrument used to measure the ratio of the voltages of the electrolytic cell and the metallic resistance in series with it. If the voltage measuring instrument is to be used as an absolute one, a potentiometer will give accurate measurements but this entails having the probe electrodes of such a nature that no variable polarization will occur during the course

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of the measurement. The choice of an electrometer which has an infinite resistance will have a determining advantage, as no polarization of the probe electrodes can occur owing to the infinite resistance of this electrometer. The employment of the obsolescent quadrant electrometer, which was used as a first choice of this type of instrument, is described in some detail. There the four metallic electrodes can be used.

Before going on to a detailed description of this electrometer it might be well to discuss the probe metallic electrodes. As indicated, tin electrodes were considered to be of considerable interest. When these were made by molding pure tin metal in wooden molds they were found to show an insignificant difference of potential when immersed in an aqueous solution of an electrolyte; small as this potential was it also showed no measurable variation with time and concentration of electrolyte. This potential difference, as will be elaborated on later, did not affect experimental observations. With platinum electrodes made out of foil or wire this difference in potential between two such electrodes immersed in a solution of an electrolyte was measurably large (0.1 volt), and was variable to the extent of 0.01 volt under certain experimental conditions; as the over-all voltage on the electrometer was 20 volts, the variation of 0.01 volt meant the accuracy would only be 1 part in 2000. However, if instead of platinum electrodes, platinum black electrodes are used, the difference of potential between two such electrodes in a solution containing an electrolyte is very much less, and therefore any variation in the accuracy attained is diminished. The same concept applies to any other electrodes that are used inasmuch as the probe electrodes must be made as uniform as possible, physically and chemically. Sample data for tin and platinum black electrodes are given after the description of the use of the quadrant electrometer as the measuring instrument in the direct current method.

The quadrant electrometer was originally designed as an instrument for the direct measurement of voltages and it must be kept in mind that in this work the quadrant electrometer is used as a null instrument comparing equal voltages. It then becomes an instrument giving a very high degree of precision, with which an accuracy of 1 in 10,000 can be obtained under our experimental conditions when the over-all voltage measured is 20 volts, which can be considerably enhanced with higher voltages. In using the quadrant electrometer to attain such accuracy it is important that measurements be made quickly to avoid drift owing to external electrostatic charge environment and to avoid any hysteresis effect in the suspension of the electrometer should it be subjected to sudden major changes. To countervene these effects a setup was arranged in such a way that the voltage on the electrometer was maintained continuously, except for the fractional second interval in which a double pole switch was manipulated so that small changes in the metallic resistance could be made. These only affected slightly the needle position as reflected on the scale, and were made to bring the null point register of the cell and the resistance box together.

Now for a detailed description of the experimental outlay. Referring to Fig. 1, the resistance  $R_1$  is adjusted until it equals the cell resistance and the electrometer reading does not change when the alternating switch D is placed across the probe electrodes A,A of the cell or the resistance  $R_1$ .

An image from a Leeds and Northrup galvanometer lamp was focused on the electrometer, which was set up on a Julius suspension. The image was in turn projected onto a scale calibrated in millimeters placed 4 meters from the electrometer. A telescope was focused on this image making possible a detection of 1 part in 10,000 when a 45-volt dry cell was used in the circuit giving approximately 20 volts across the electrometer.

The electrolytic cell was placed in a water bath, the temperature of which was con-

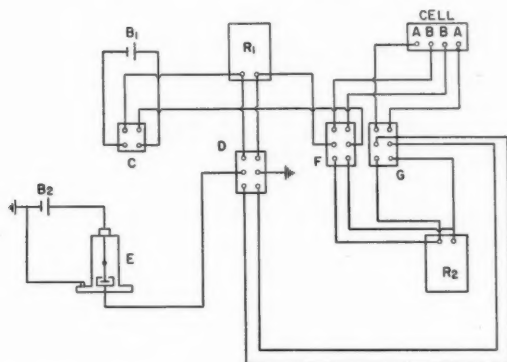


FIG. 1.

trolled to  $1/100^{\circ}\text{C.}$ , and the electrodes A,A and B,B were connected. The current flowing from dry cell  $B_1$  through switch C and resistance  $R_1$  passes through the cell. The measurements are then made by alternating switch D from the cell side (probe electrodes A,A) to the resistance  $R_1$  side, and then obtaining a null position on the scale by varying resistance  $R_1$ .

The simplest way of maintaining the voltage on the electrometer, and thus maintaining the image on the screen, would be to have a continuous passage of the current through the circuit including the cell. With time, electrolysis would take place owing to this continuous passage of current, although it is greatly reduced by the design of the cell (shown later). To eliminate this, switches F and G are employed, which are double pole, double throw switches connected together and reversed simultaneously. Resistance  $R_2$  is adjusted to the cell resistance and when switches F and G are reversed the current bypasses the cell through resistance  $R_2$ . By this means the current passes through the cell only during the time when measurements are being made, which is of the order of less than 1 minute. The voltage is maintained at any time on the electrometer within the fractional second of alternating switches F and G. This makes the quadrant electrometer, with all its disposition to take up vagrant electrostatic voltages, a null instrument of the high degree of accuracy outlined above.

When the sensitivity of the electrometer is arranged to measure a variation of 1 part in 10,000, it is important that no variation in voltage occurs in the circuit during the time required for making measurements. During this time interval it was proved that the voltage of the dry cell remained constant. There remains the question of any inherent voltage between the probe electrodes, which would not affect the measurements, if it remained constant; and as was pointed out previously between tin electrodes prepared as described and between platinum black electrodes, such voltages are insignificant, and therefore no variation could be expected or was found.

Two platinum, tin, or tungsten probe electrodes when freshly cut exhibited a difference of potential in an electrolytic solution and were variable with time and external conditions; where such probes are used the accuracy of conductivity measurements may be reduced to 1 part in 500 under extreme conditions. Platinum electrodes can also be molded and would probably be as effective as molded tin. With tungsten this cannot be done, but still for most purposes where the nature of the electrolyte requires tungsten (aqua regia solutions) a sufficient degree of accuracy for the purpose of the measurements can be obtained.



## CELL

In Fig. 2 the design of the cell is shown. A,A are the probe electrodes and B,B are the current carrying electrodes, all of which are made of pure tin as previously described, or of platinum black (not shown in the diagram). In this arrangement advantage is taken of the work of Ives (6) to ensure that the physical position of the probe electrodes will not affect the cell constant. The bulbs C,C below the current carrying electrodes are to ensure that any slight change in concentration due to electrolysis around the current carrying electrodes would not permeate into the main body of the cell where the conductivity is being measured. In this connection it may be recorded that it was found that over a period of 5 minutes during which a continuous current was passed through the cell, no measurable changes in resistance due to such electrolysis were found to occur. This time factor is very much below that which is involved in making our measurements.

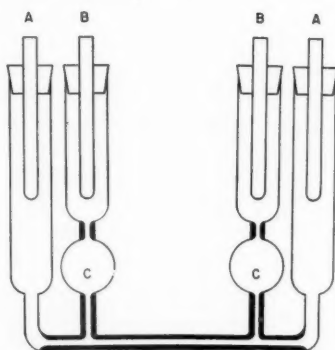


FIG. 2.

## PREPARATION OF SOLUTIONS

Three solutions, 0.1, 0.05, and 0.01 *N* in potassium chloride, were made up by volume using reagent grade potassium chloride and taking all the experimental precautions which are normally taken to ensure the accuracy of the concentration. Corrections for temperature and volume showed that the solutions used had actual concentrations of 0.09990, 0.049950, and 0.009990 *N* potassium chloride. The data for aqueous potassium chloride conductivity have been well established by Shedlovsky (9) and the cell constants were calculated in the usual way using these data.

## RESULTS

When the quadrant electrometer system, as outlined above, was used to measure a known metallic resistance in place of the electrolytic cell, an absolute accuracy of 1 part in 10,000 was obtained over a considerable range of resistance. The test consisted of having someone set the resistance box (replacing the cell) at a definite resistance and then having the observer make a measurement. At first, some difficulty was encountered in attaining this degree of accuracy when the electrolytic cell (replacing the metallic resistance) was measured. However, when the probe electrodes were conditioned as described, the same degree of accuracy was attained as in the measurement of the metallic resistance. It now remains to tabulate a sample set of experimental observations, which



confirm the claim that the particular experimental procedure involving probe and current carrying electrodes made of any desired material will give results to a high degree of accuracy.

In Table I are given the data which have been corrected for the conductivity of the solvent (water). This was measured conveniently by the direct current method employing a cell having a very much lower cell constant than the one used in this work. This was accomplished by using a glass tube between the probe electrodes 50 times larger in diameter than the one illustrated in Fig. 2, which was 2-millimeter capillary tubing.

It can be seen that with tin electrodes an accuracy of 1 part in 7000 and with platinum black electrodes of 1 part in 5000 was attained.

TABLE I

<i>c</i>	<i>R</i>	<i>R</i> average	<i>K</i>	<i>K</i> average
Tin probes				
0.09990	27,644 27,644 27,643	27,644	356.10	
0.049950	53,445 53,443 53,446	53,445	356.08	356.10
0.009990	251,810 251,815 251,810	251,808	356.13	
Platinum black probes				
0.09990	27,633 27,633 27,633	27,633	355.99	
0.049950	53,435 53,433 53,433	53,433	356.00	356.02
0.009990	251,655 251,650 251,650	251,652	356.06	

*c*—Concentration.

*R*—Resistance.

*K*—Cell constant.

#### DISCUSSION

The authors believe that an even higher degree of accuracy by the method described can be obtained if more accurate measurements are made of the conductivity of the solvent. This conductivity depends on the time that the electrolytic solution used as a standard is in contact with glass containers. A teflon cell can and has been used in certain experiments, and it is considered that if the standards are made up in teflon containers it will be possible to get reproducible results to even better than 1 part in 10,000. Taking the 0.09990 and the 0.049950 *N* solutions as in Table I, it is seen that a very high degree of relative accuracy is attained.

The accuracy required by the investigator is dependent on the fact that an accurate determination of the solvent conductivity will be of greater importance when solutions of 0.009990 *N* are used.

Instead of using a quadrant electrometer, which embodies the requirement of having an infinite resistance, a more simple device can be used. This consists of a charged metallic fiber subject to displacement between two electrodes leading to alternately the probe electrodes and the metallic resistance in series. The first electrometer of this nature showed it was possible to make null measurements giving an accuracy of 1 part in 1000. It is considered that this accuracy can be considerably enhanced by changing the dimensions involved in this instrument, and a study of this is underway.

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# THE PHOTOLYSIS OF METHYL CYANIDE AT 1849 Å<sup>1</sup>

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## ABSTRACT

The photolysis of MeCN has been investigated under a considerable range of conditions and a mechanism proposed which accounts satisfactorily for the products found, viz. H<sub>2</sub>, HCN, C<sub>2</sub>N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>5</sub>CN. Two primary processes occur



of which the former is apparently the more important. HCN is formed predominantly by an H atom abstraction of the CN group which is believed to occur through addition to the unsaturated bond with the formation of an unstable imine radical. This and similar intermediates formed by other radicals are proposed to account for several anomalies found in the photochemistry of nitriles.

A brief investigation of the photolysis of carbonyl cyanide is reported.

## INTRODUCTION

The photochemistry of the nitriles has received very little attention, undoubtedly because the nitriles are generally transparent well into the Schumann region. Certainly no direct photolysis of a nitrile has been reported previously in the literature beyond a simple spectrographic investigation of MeCN and EtCN by Terenin and Neujmin (1), who established the presence of excited CN radicals in the far ultraviolet photolysis of these molecules and concluded that excitation is followed by dissociation of the carbon-carbon bond. The possibility of a system of CN reactions parallel to those of CH<sub>3</sub> in which HCN and C<sub>2</sub>N<sub>2</sub> would be formed in an analogous manner to the well-known methane- and ethane-forming reactions of CH<sub>3</sub> was of considerable interest when we undertook the present work. In view of the unsaturated nature of the CN group this conjecture was quite unjustified and the reaction proved to be considerably more complex and unusual.

## EXPERIMENTAL

The ultraviolet absorption of MeCN lies entirely within the Schumann region. The 1849 Å mercury resonance line roughly coincides with the long-wave edge of a band which occurs between 1600 Å and 1800 Å (Platt and Kleven's (2)). Although this marginal absorption is unfortunately weak, the mercury arc conveniently compensates by providing a relatively intense light source. The decisive advantage of the mercury arc, however, proved to be the reasonably high transparency of fused quartz to 1849 Å, which allowed the use of a conventional quartz cell; this is an important consideration because of the accumulation of polymer in the MeCN photolysis. The only effective method of removing this obscuring deposit was by heating the cell to red heat in the presence of oxygen.

The use of the 6<sup>1</sup>P<sub>1</sub> mercury resonance line, of course, necessitates the complete absence of mercury vapor from the reaction cell, and a mercury-free system employing an oil

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diffusion pump backed by a previously unused Welsh Duoseal pump was provided for the reagents and cell. The problem of transferring the reaction products to the analysis train, a separate mercury-containing vacuum system, was solved very satisfactorily by bridging the two lines with a small single-stage diffusion pump operating continuously with stable, inert Dow 703 silicone oil. The effectiveness of this arrangement in preventing back-diffusion of mercury vapor and the subsequent contamination of the reaction system was variously proved. At regular intervals both ethane and MeCN were illuminated with the 2537 Å resonance line using a Corning 7910 filter to cut off 1849 Å; at no time during the investigation was the mercury-photosensitized production of  $H_2$  detected even after an illumination period of several days. The efficiency of the transfer diffusion pump in preventing back-diffusion was exhibited more directly, perhaps, by the complete lack of absorption of 1849 Å in the evacuated cell when the bridge section between the cell and the mercury system was opened. It should be emphasized that such drastic measures are necessary if a mercury-free system is to be obtained. The conventional use of gold foil as a mercury trap is almost totally ineffective. It is our experience that if mercury vapor has ever entered a vacuum system it can never be completely removed.

The reaction cell was the usual cylindrical quartz vessel, 15 cm. long and 252 cc. volume, mounted centrally in a split aluminum block furnace and attached to the vacuum line through a quartz-pyrex graded seal. A low pressure mercury arc, shaped into a flat spiral of somewhat greater diameter than the cell, was sealed into one end of the furnace with a solid plug of asbestos so that maximum intensity could be obtained by operating in a stream of nitrogen (to avoid absorption by oxygen). For this purpose, liquid nitrogen was boiled at a controlled rate from a 3-liter Dewar flask by an immersion heater. The cool gas was introduced into the furnace from behind the lamp, cooling it and incidentally helping to balance the temperature gradient caused by the lamp. The 1849 Å intensity is increased in this way by as much as a factor of 10, perhaps partly because of the efficiency peak of this type of lamp at about 55° C. Collimation was impracticable and for optimum operating conditions the lamp was spaced about 5 cm. from the cell window. The cell temperature, controlled through a 10-amp. Variac auto transformer operating from a Sorensen voltage stabilizer, was uniform to within 2° and stable to  $\pm 2^\circ$  over long periods of time. Cell pressures were measured by a null point quartz spiral manometer with a mercury manometer reference accurate to  $\pm 0.5$  mm.

The analytical line consisted of mercury cutoffs throughout with the exception of the bridge connection from the reaction cell which was isolated by a stopcock and led directly into a U-trap, which in practice was cooled with liquid nitrogen whenever the bridge stopcock was open, although it was shown that the oil diffusion pump was effective by itself in preventing mercury from diffusing into the mercury-free line. Two Leroy stills and a solid nitrogen trap followed the U-trap to effect fractional distillation of the products, which were pumped into the gas burette by a small two-stage mercury diffusion pump. The burette, which was stopcock-free, could be evacuated through cutoffs by either of two Töpler pumps, one for cycling the products through hot CuO and the other for filling sample tubes for mass spectrometric analysis. The CuO was maintained at 570° C. in a fused silica U-tube in order to oxidize methane to  $CO_2$ . At this temperature the methane oxidation rate was very slow, taking 12 hours to effect completion, while hydrogen was almost instantaneously oxidized with negligible attack on methane. This procedure permitted the convenient analysis of a mixture of  $H_2$ ,  $CH_4$ , and  $N_2$  with high accuracy as proved by standard mixtures. Dead space was kept to a minimum by using capillary tubing for the U-trap and connecting tubing. Higher CuO temperatures must be avoided to prevent  $O_2$  production.

Methyl cyanide was treated with KOH to remove traces of HCN, distilled into the mercury-free line through  $P_2O_5$ , the middle third being preserved in a stopcocked reservoir, and thoroughly outgassed. A clean mass spectrum was obtained, but as a further precaution a sample of the MeCN was fractionated from a Leroy still into three samples which were compared on the mass spectrometer; no significant difference in the three spectra was observed.

The runs were carried out with maximum light intensity rather than constant absorbed intensity, since the intensity was generally so low that illumination periods ranged from 4 to 20 hours. Even in the longest runs less than 5% conversion of MeCN occurred. The gaseous products were identified by the mass spectrometer as HCN,  $C_2H_5CN$ ,  $H_2$ ,  $C_2N_2$ ,  $CH_4$ , and  $C_2H_6$  with traces of  $C_2H_2$ ,  $C_2H_4$ , and  $C_3H_8$ . Of other possible products,  $N_2$  and  $NH_3$  were specifically sought but never detected within our range of conditions.

The products were separated by low temperature fractionation into three distinct fractions:

(1)  $H_2$  and  $CH_4$  were collected as the volatile fraction at  $-210^\circ C$ . and subsequently analyzed by CuO at  $570^\circ C$ . at which temperature  $H_2$  was oxidized and determined by difference in a single pass.  $CH_4$  was determined as  $CO_2$  after 12 hours in contact with CuO as a check against the presence of  $N_2$ . The  $CO_2$  invariably reproduced the  $CH_4$  measurement to within 0.5%;  $N_2$  was not observed.

TABLE I

Press., mm.	Temp., ° K.	[CH <sub>3</sub> CN], × 10 <sup>-18</sup> molecules per cc.	$R_{CH_4}$							$R \frac{1}{2} C_2H_6 [MeCN]$ , × 10 <sup>14</sup> molecules <sup>-1</sup> cc. <sup>-1</sup> sec. <sup>-1</sup>
			$R_{CH_4}$	$R_{H_2}$	$R_{C_2H_6}$	$R_{HCN}$	$R_{C_2N_2}$	$R_{H_2}$	$R_{C_2N_2}$	
			× 10 <sup>-10</sup> molecules/cc./sec.							$R_{HCN}$
23.0	332	0.668	1.225	1.440	3.24	9.65	0.885	0.127	0.092	13.2
63.0	332	1.830	3.88	3.57	7.00	24.1	2.78	0.145	0.115	8.02
111.3	332	3.25	7.39	5.61	9.84	33.1	2.25	0.224	0.083	7.23
107.2*	332	3.12	1.12		0.714					3.04
194.7	332	5.65	12.50	8.20	11.75	39.9		0.205		6.45
26.5	373	0.686	2.60	2.25	2.23	16.9	0.54	0.133	0.032	25.4
47.0	371	1.22	6.27	3.80	6.06	27.6	1.98	0.137	0.072	20.9
61.8	369	1.62	8.52	5.20	7.31	39.2	4.50	0.133	0.115	19.4
79.2	369	2.07	11.52	6.44	8.86	47.2	4.50	0.136	0.096	18.7
105.0	375	2.705	16.00	6.92	9.03	52.1	5.13	0.133	0.099	19.6
26.2	477	0.530	13.68	2.49	1.775					194
35.1	474	0.716	24.05	4.85	2.38	44.1	4.61	0.110	0.104	218
43.4	473	0.885	34.2	6.16	4.00	63.0	6.43	0.098	0.102	193
50.5	474	1.030	41.3	7.64	4.18	66.8	7.69	0.114	0.115	201
81.0	473	1.653	67.9	11.44	5.74					171
104.0	474	2.12	82.1	13.3	6.47					153
39.0	458	0.823	23.1	4.34	2.92					164.0
71.5	450	1.536	43.0	8.42	4.78	65.0	7.20	0.130	0.111	128.5
164.5	460	3.46	77.4	11.94	5.01	95.0	14.0	0.126	0.148	99.8
242	453	5.16	128.6	19.5	7.09	145.0	18.8	0.134	0.130	93.7
290	460	6.10	150.3	22.0	4.68	165	11.4	0.146	0.069	116.0
310	456	6.56	146.3	26.2	6.42	147.5	23.2	0.177	0.158	88.2
26.7	582	0.438	43.5	5.83	0.606	37.8	7.83	0.154	0.207	1275
33.7	579	0.563	39.8	6.04	0.271	35.9	7.74	0.168	0.215	1353
46.4	582	0.770	52.4	7.13	0.252	48.1	8.72	0.148	0.181	1350
62.1	582	1.030	69.9	10.23	0.305	61.4	11.08	0.167	0.180	1230
77.6	581	1.289	98.4	12.22	0.295	79.5	14.61	0.154	0.184	1405
106.2	580	1.770	102.2	12.78	0.250	91.0	15.4	0.140	0.169	1158
133.2	583	2.21	157.8	13.80	0.417	124.0	23.1	0.111	0.186	1100

\* Intensity = 7% preceding run.

(2)  $C_2H_6$  containing only traces of  $C_2H_4$  was usually checked by the mass spectrometer.

(3) HCN and  $C_2N_2$  were collected together for mass spectrometric analysis by distillation from the first Leroy still at a bottom temperature of  $-80^\circ C$ . through the second Leroy still at  $-100^\circ C$ . To ensure complete collection, distillation was continued well into the MeCN fraction.  $C_2H_5CN$  was always evident on the mass spectrum as it came over with the MeCN. Although it was shown to be a major product, approximately 80% of HCN concentration, satisfactory separation was not practical.

The results of a series of runs over a pressure range of 26 mm. to 300 mm. and temperatures from  $55^\circ C$ . to  $300^\circ C$ . are expressed as rates of formation in Table I.

In addition to the gaseous products some unidentified solid remained on the cell walls, except at the highest temperatures, in sufficient quantity to decrease the light intensity by as much as 20% by the end of the run. It proved necessary to burn the polymer from the cell walls by introducing air or oxygen after each run and this prevented the use of a more efficient assembly of combined lamp and cell. Furthermore it restricted experiments to a normal quartz cell and made it impracticable to use thin sucked-in windows, thus preventing investigation at shorter wavelengths.

The  $CO_2$  formed by total combustion of the solid residue was found to be roughly equal to twice the HCN formed in the reaction; incidentally, no observable pressure change occurred during any of the runs; hence it appears likely that the solid product is largely dinitrile. Certainly little polymerization of MeCN takes place.

Accurate quantum yields were virtually impossible to obtain since  $I_{ab}$  is almost immeasurable and the incident intensity is unstable over long periods. However, using  $N_2O$  as an actinometer,  $\Phi_{HCN}$  was shown to be of the order of unity. Intensity studies suffered similarly in crudity, yet the most reliable results obtained (Fig. 1) show clearly that

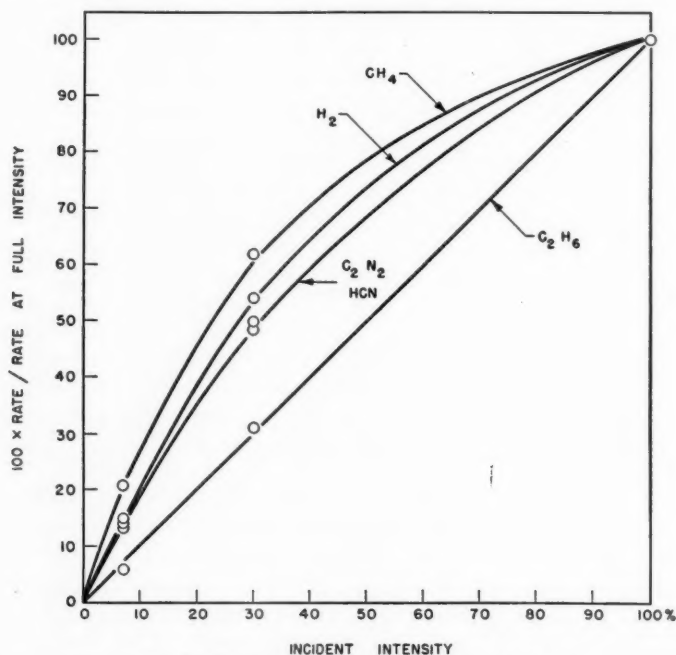


FIG. 1. Effect of intensity on formation of products.



$R_{C_2H_6}$  varies linearly with  $I_{ab}$ , in a quite different manner from the behavior of  $R_{HCN}$ ,  $R_{C_2N_2}$ ,  $R_{CH_4}$ , and  $R_{H_2}$  which are more nearly proportional to  $\sqrt{I_{ab}}$ . (The incident intensity is used in Fig. 1. In view of the weak absorption, however, it is strictly proportional to the absorbed intensity.)

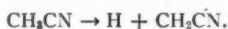
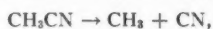
Some experiments were made to investigate the part played by H atoms in the MeCN photolysis.  $H_2S$  and  $D_2S$  were photolyzed in the presence of MeCN using the 2537 Å region of a Hanovia S500 lamp. The mercury photosensitized decomposition of  $H_2$  and  $D_2$  in the presence of MeCN was also carried out in an auxiliary cell on the mercury system using the 2537 Å resonance line isolated from 1849 Å by a Corning 7910 filter. Incidentally, little direct photosensitized decomposition of MeCN occurs although the quenching cross-section is comparable to that of  $H_2$ . In both cases, all the products of the direct photolysis were found with the significant exception of  $C_2N_2$ . A material balance showed that  $R_{HCN} = (R_{CH_4} + 2R_{C_2H_6})$  to within 5%, which can be accounted for only by a reaction such as



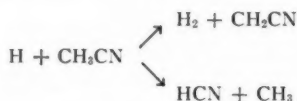
a conclusion reached also by Forst and Winkler (3).

#### DISCUSSION

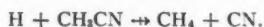
At 1849 Å two primary processes are energetically possible:



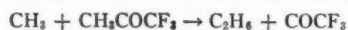
From the nature of the products it is evident that all four radicals are involved in the reaction mechanism. Only  $CH_2\dot{C}N$  would normally be expected to arise from secondary reactions as a result of H abstraction from the parent molecule; however in the present system  $CH_3$  radicals have been proved to be liberated by an H atom attack on MeCN to form HCN.



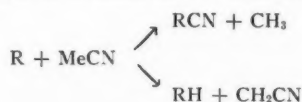
On the other hand neither H atoms nor CN radicals are accounted for by secondary reactions and must be primary species. The absence of  $C_2N_2$  in the H atom sensitization of MeCN precludes the third possibility of H atom interactions:



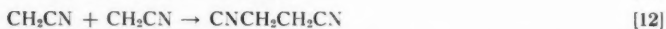
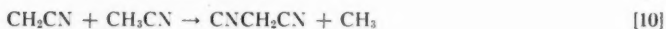
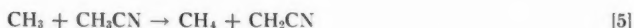
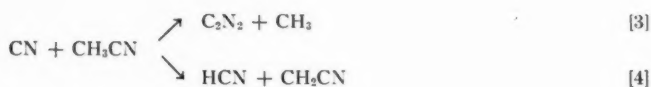
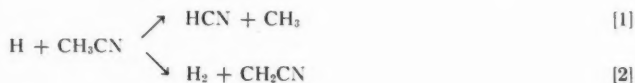
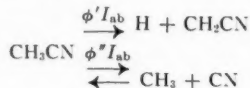
Theoretically this type of reaction is most unfavorable, since it involves the attack of a highly shielded atom and although it has been recently invoked in the reaction



(Ref. (4)), our observations are consistent with the current view. The 'abstraction' of the CN group on the other hand almost certainly results from the addition of an H atom to the group with its easily accessible  $\pi$ -bonds, to form an unstable imine radical. Bentley and Wijnen (5) observed a similar reaction with  $CH_3$  radicals and in the present work there is positive evidence of the formation of  $C_2N_2$  by 'abstraction'. It is therefore evident that the reaction is not limited to H atom attack but is of more general occurrence:

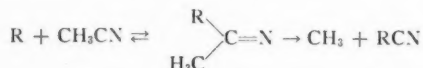


Both primary processes are important in the photolysis of MeCN, although the evidence favors the predominance of a C—H split. It is impossible to arrive at a unique mechanism on the basis of the information available, but the following mechanism appears reasonable and is in general agreement with the facts:



Direct evidence for reaction [1] was obtained in the H- and D-atom investigations, as previously mentioned, and we infer from the temperature independence of the ratio  $R_{\text{H}_2}/R_{\text{HCN}}$  (Table I) that the activation energy is very close to that of reaction [2]. It can only be assumed that reactions [3] and [4] are similar in this respect also. The evidence for reaction [3] is somewhat less direct; however, it is apparent that  $\text{C}_2\text{N}_2$  production does not kinetically parallel that of  $\text{C}_2\text{H}_6$ . The intensity dependence of  $R_{\text{C}_2\text{N}_2}$  is quite different from the linear relationship of  $R_{\text{C}_2\text{H}_6}$  (see Fig. 1) and is more characteristic of abstraction reactions. Furthermore,  $\text{C}_2\text{N}_2$  production increases with higher temperatures in direct contrast to  $\text{C}_2\text{H}_6$  production, a fact that can be explained only by a competition between a high temperature reaction [3] and a low temperature combination reaction [7] in the formation of  $\text{C}_2\text{N}_2$ .

The removal of the CN group in reactions [1] and [3] is almost certainly not a true abstraction reaction. Only the  $\pi$ -bonds of the nitrile group are open to radical attack resulting in an unstable excited addition complex which can either split off the  $\text{CH}_3$  group or back-dissociate.



When R is H or CN the forward reaction is exothermic by 10 kcal. and 8 kcal., respectively.

The addition product intermediate, which is an imine radical, apparently has a short lifetime, since no stable imine end product has been detected. It may, however, be a source of methane by reaction [9]. It is evident from the results in Table I that reactions

[5] and [6] do not completely describe the methane-ethane relationship. There is a small but real influence of pressure on the ratio  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}[\text{MeCN}]$  (Fig. 2) which does not appear in the photosensitization of MeCN with acetone- $d_6$  carried out by Wijnen (6). The Arrhenius plot of Wijnen's results gives a linear slope of 10 kcal. for the abstraction of H from MeCN. In the direct photolysis a 10-kcal. slope is found only at high temperatures while at 55° C. it has tailed off to only 4 kcal. (Fig. 3). There is some parallel here to the photosensitization of HCN with acetone- $d_6$  by Eaton and Wijnen (7), in which an abnormally low activation energy was found for H abstraction. Apparently the same intermediate is formed by the addition of  $\text{CH}_3$  to HCN as obtains with H and  $\text{CH}_3\text{CN}$ , which must take part in the methane reaction. Since this radical does not break down to form  $\text{CH}_4$  and a CN radical, it must act by providing a readily abstractable hydrogen. Further evidence of a radical-radical methane step such as reaction [9] is the marked intensity dependence of  $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}[\text{MeCN}]$  (Table I) at 55° C. which does not occur at higher temperature.

$\text{C}_2\text{H}_5\text{CN}$  was identified as a product by the mass spectrometer and can be accounted for only by reaction [8], which is analogous to the  $\text{C}_2\text{H}_5\text{COCH}_3$ -producing reaction in the photolysis of acetone. Reactions [11] and [12] in the absence of direct identification are included in the mechanism as reasonable analogues of the acetone photolysis and of

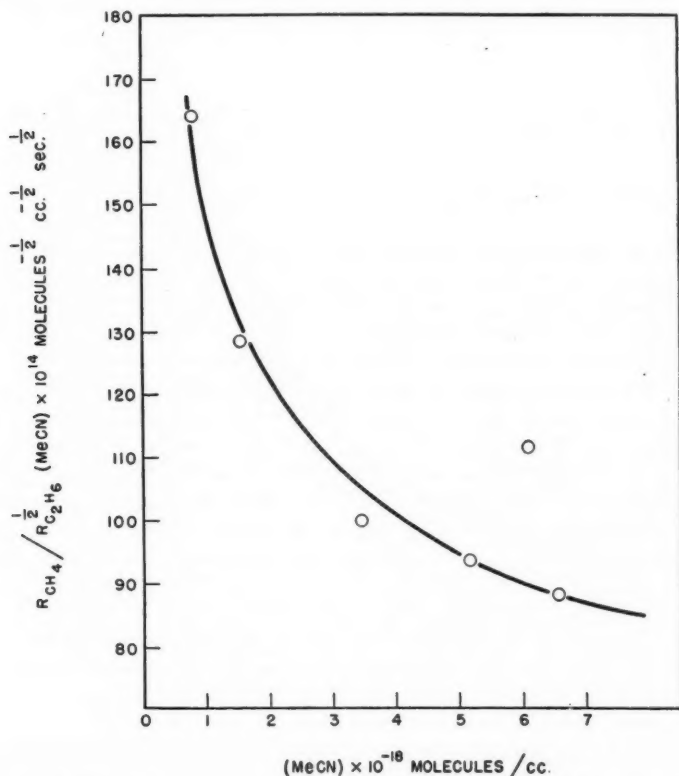


FIG. 2. Effect of pressure on production of methane and ethane. Temperature ~456° K.

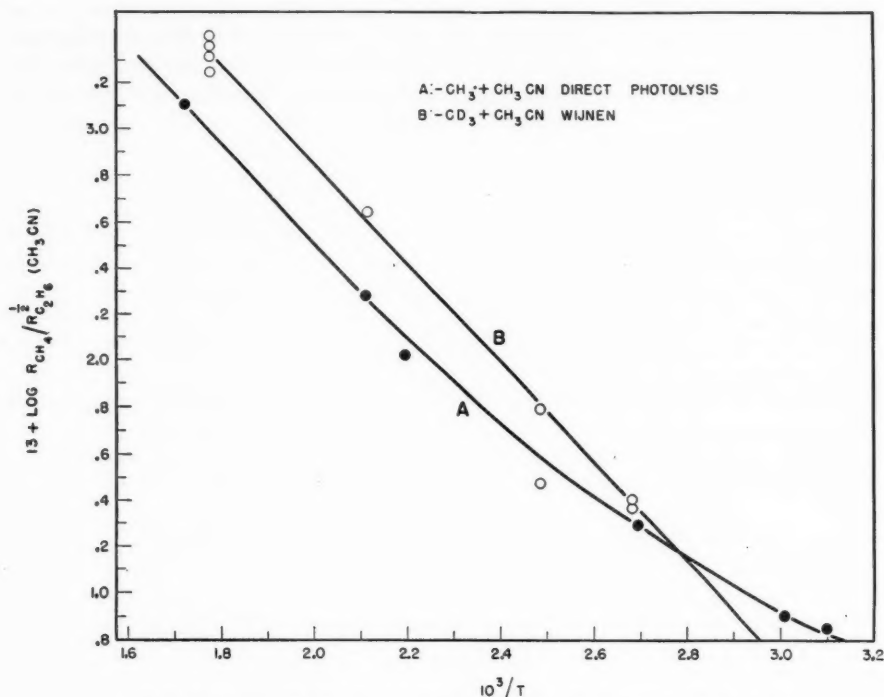


FIG. 3. Arrhenius plot for the reaction of methyl radicals with methyl cyanide.

reaction [8]. However, there is some evidence that much of the deposit on the cell walls is dinitrile. The absence of the deposit in high temperature runs is deemed significant in view of the boiling points of the two nitriles, which are of the order of  $250^\circ\text{C}$ . Reaction [10] has been retained for symmetry although it is unlikely to be extensive since the two carbon-carbon bonds in the intermediate would be very similar in strength.

We believe it is of interest to report on some experiments with  $\text{CNCOCN}$ , which has a similar absorption spectrum to that of acetone and which was available through the kindness of Dr. Leitch of this laboratory. It was an obvious choice as a possible source of CN radicals which would have been very useful in the present investigation. However, there are serious difficulties which render  $\text{CNCOCN}$  useless as a photosensitizing agent. Very extensive polymerization occurs in photolysis which apparently starts homogeneously since the illuminated volume of the cell becomes almost immediately filled with a fine suspension of particles. Furthermore,  $\text{CNCOCN}$  apparently undergoes a molecular reaction with water to form 1 mole of  $\text{CO}_2$  and 2 moles of  $\text{HCN}$ . This effect appeared to be virtually inescapable as considerable care had been taken to outgas the vacuum system.  $\text{C}_2\text{N}_2$  and  $\text{CO}$  were certainly products of the reaction. However, in view of the difficulties just mentioned, nothing can be stated regarding a mechanism.

The authors are greatly indebted to Dr. K. O. Kutschke for much helpful advice and criticism.

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# THE LIMITING EQUIVALENT CONDUCTANCES OF AMMONIUM CHLORIDE, AMMONIUM BROMIDE, AND AMMONIUM NITRATE AT 35.00° C.<sup>1</sup>

A. N. CAMPBELL AND E. BOCK<sup>2</sup>

## ABSTRACT

The limiting equivalent conductances of ammonium chloride, ammonium bromide, and ammonium nitrate as well as the limiting ionic conductances of the ammonium and nitrate ions were determined at 35° C. with a probable error of 0.05%. The values found were  $\Lambda_{\text{NH}_4\text{Cl}}$  180.97 mhos,  $\Lambda_{\text{NH}_4\text{Br}}$  182.73 mhos,  $\Lambda_{\text{NH}_4\text{NO}_3}$  174.21 mhos,  $\lambda_{\text{NH}_4^+}$  88.73 mhos, and  $\lambda_{\text{NO}_3^-}$  85.48 mhos. These values were obtained by the application of the Shedlovsky method of extrapolation to equivalent conductance data, which had been corrected for the hydrolysis of the ammonium ion.

Observed equivalent conductances of aqueous solutions of ammonium nitrate at 35° C., in the concentration range from 0.0002 *N* to 10 *N*, have been compared with those calculated by means of the Wishaw-Stokes and Falkenhagen-Leist equations. The Wishaw-Stokes equation was found to give better agreement with experiment than the Falkenhagen-Leist equation.

In order to apply the conductance equations of Wishaw and Stokes (1) and of Falkenhagen and Leist (2) to conductance data obtained in this laboratory for ammonium nitrate at 35° C., it is necessary to know  $\Lambda_0$ , the limiting conductance of ammonium nitrate at this temperature, and we therefore undertook to determine it. At the same time, we thought it would be interesting to determine the limiting conductances of the individual ions, viz.  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . This information results at once from the limiting conductance of the salt, if the transference numbers are known. Since, however, no experimental values of the transference numbers of the ions of ammonium nitrate are given in the literature (for 35° C.), we approached the problem by making experimental determinations of the limiting conductances of ammonium bromide and of ammonium chloride. Since the conductances of bromide and of chloride ions are known accurately at 35° C., it was possible to obtain the conductance of ammonium ion and of nitrate ion.

## EXPERIMENTAL TECHNIQUE

The technique of measurement of conductance in very dilute solutions has been worked out in great detail, over the years, and it is to be found in works of reference. Nevertheless, some reference to the methods used by us is necessary, if only to prove that the necessary precautions were taken.

### A. Purity of Materials

#### 1. Salts

Fisher certified reagents were used; they were recrystallized twice from conductance water, dried at 90° C., and kept over sulphuric acid until needed. The potassium chloride used for cell constants was, in addition, ignited before use. Objection has been made to fusing the potassium chloride on the ground that a minute trace of hydrogen chloride may be expelled from the moist salt, leaving the residue alkaline, but direct testing showed that this did not happen with us.

#### 2. Conductance Water

A good quality distilled water was passed through an Amberlite MB-3 ion exchange column. When the effluent water was exposed to the air, its specific conductance increased,

<sup>1</sup>Manuscript received September 25, 1957.

<sup>2</sup>Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Manitoba.

<sup>3</sup>Holder of the Cominco Fellowship of the Consolidated Mining and Smelting Company of Canada, to whom we are also indebted for a grant for the expenses of the research.



rapidly at first and then more slowly, as the water became saturated with carbon dioxide from the air. The final value obtained, for the so-called "equilibrium water" (usually about  $1 \times 10^{-6}$  mhos), was the one used when applying the solvent correction to the observed specific conductances of the solutions, since the solutions were prepared and all measurements made in contact with the atmosphere.

## B. Conductance Measurements

### 1. The Bridge

A Leeds and Northrup Campbell-Shakelton bridge was used, for which the makers claim an accuracy of 0.05%. A tuned telephone headpiece in series with a two-stage resistance-coupled amplifier served as detector; high sensitivity with low power input was thus obtained.

### 2. The Conductance Cells

Three cells were used, all of the design recommended by Jones and Bollinger (3). The electrodes were lightly platinized. The cell constants varied from 0.55032 to 46.1383.

### 3. Preparation of Solutions

(a) *Concentrations from 0.1 M to 0.005 M.*—A quantity of salt (never less than 2 g.) was weighed to 1/10 mg. The salt was transferred to a pyrex flask of 1-liter capacity, water added to give approximately the desired concentration, and the weight of the solution determined to the nearest 5 mg. All weighings were reduced to vacuum. The density was then determined.

(b) *Concentrations from 0.005 M to 0.0005 M.*—Twenty to fifty grams (weighed to 0.1 mg.) of a more concentrated solution were diluted with approximately 1600 g. water. The resulting solution was weighed to the nearest 5 mg., and the normality calculated from the known amounts of salt and water. It was not necessary to know the density at these concentrations, since the density of the solutions is not appreciably different from that of water.

### 4. Measurement of Equivalent Conductance

The cells were allowed to remain in the thermostat for  $\frac{1}{2}$  hour after filling, before commencing the measurements. Readings of conductance were then taken at 5-minute intervals for another  $\frac{1}{2}$  hour. For solutions stronger than 0.001 M, no change in conductance with time was observed, but with solutions more dilute than 0.001 M, as well as with conductance water, a slow but steady increase of conductance with time was observed. For the most dilute solutions the change amounted to 0.02% and for water to 0.1%.

In order to correct for the increase of conductance with time, conductance readings were plotted against time and the curve extrapolated to zero time. The extrapolated value was taken as the "true" conductance of the solution. That this procedure was sound is borne out by the fact that conductance measurements of solutions having identical concentrations showed agreement to better than 0.01%. Moreover, no less than seven determinations of the conductances of potassium chloride solutions, ranging in concentration from 0.001 M to 0.0005 M, were made and the results compared with those obtained by Gordon (4). The comparison was effected by calculating  $\Lambda_0$  from the following empirical equation proposed by Gordon, using experimental concentration and conductance data:

$$\Lambda_0 = \Lambda_0' - Bc + Dc \log c. \quad [1]$$

In all seven instances the values of  $\Lambda_0$  did not differ from that reported by Gordon by more than 0.04%. In view of the fact that Gordon used a fundamentally different method of measurement (direct current method) and that equation [1] is claimed to represent conductance data to within 0.02 to 0.03%, the agreement obtained is quite satisfactory.

### 5. Thermostat

The thermostat was oil-filled and controlled to  $0.002^{\circ}\text{C}$ . Temperature was read on a Beckmann thermometer, which was calibrated periodically against a platinum resistance thermometer.

### EXPERIMENTAL RESULTS

The main experimental results are summarized in Table I. The table contains the specific and equivalent conductances and densities of aqueous solutions of ammonium nitrate, of ammonium chloride, and of ammonium bromide at  $35.00^{\circ}\text{C}$ .

TABLE I  
SPECIFIC AND EQUIVALENT CONDUCTANCES AND DENSITIES  
OF AQUEOUS SOLUTIONS, AT  $35.00^{\circ}\text{C}$ .

Concentration, moles/liter $\times 100$	Specific conductance, $\text{mhos cm.}^{-1} \times 10^6$	Equivalent conductance, mhos	Density, g./ml.
A. Ammonium nitrate			
7.7601	11584.2	149.28	0.99643
6.1204	9266.2	151.40	0.99589
5.0620	7743.9	152.98	0.99555
4.4589	6867.1	154.01	0.99545
3.6873	5733.4	155.49	0.99522
3.0658	4807.69	156.82	0.99505
2.3010	3656.50	158.91	0.99443
0.46208	771.293	166.92	—
0.21946	371.589	169.32	—
0.12959	220.960	170.50	—
0.10578	180.831	170.95	—
0.060330	104.719	171.86	—
0.058302	100.261	171.97	—
0.050534	86.929	172.02	—
0.025730	44.494	172.92	—
B. Ammonium chloride			
8.4588	13185.881	155.88	0.99566
6.6522	10504.926	157.92	0.99533
5.0333	8056.365	160.06	0.99513
4.3262	6975.550	161.24	0.99483
3.8014	6168.520	162.27	0.99474
3.2216	5265.409	163.44	0.99462
1.7050	2856.084	167.42	0.99449
0.18328	323.517	176.52	—
0.12245	217.023	177.23	—
0.086642	154.114	177.88	—
0.079040	140.809	178.15	—
0.047689	85.291	178.85	—
0.043436	77.816	179.15	—
C. Ammonium bromide			
7.1797	11467.8	159.72	0.99808
6.3503	10204.7	160.70	0.99770
4.8576	7904.9	162.73	0.99668
4.3820	7163.5	163.47	0.99642
3.7305	6139.5	164.58	0.99611
2.2073	3709.23	168.04	0.99519
1.9430	3280.19	168.82	0.99509
0.26811	475.137	177.22	—
0.17723	315.892	178.24	—
0.17037	303.815	178.33	—
0.096063	172.393	179.46	—
0.085742	154.112	179.74	—
0.065003	117.124	180.18	—
0.036822	66.624	180.94	—
0.025495	46.275	181.51	—

## DISCUSSION OF RESULTS

Any attempt at direct determination of degree of accuracy, as apart from reproducibility, is exceedingly laborious and, in the end, the figure arrived at is always somewhat doubtful. We thought it better, therefore, to estimate our accuracy by comparing our results for the limiting conductances of potassium chloride at 25° C. and at 35° C., and for ammonium chloride at 25° C., with the values reported in the literature. These salts were chosen because their limiting conductances have been determined by highly reputable workers, who claim an experimental accuracy of 0.01%.

For the limiting conductance of potassium chloride at 25° C., Shedlovsky (5) reports a value of 149.85 mhos. Our determination gave 149.90 mhos; the discrepancy is 0.05 mhos or 0.03%. Gordon (4) obtained 180.42 mhos for potassium chloride at 35° C.; we obtained (for the limiting conductance) 180.45 mhos, a difference of 0.03 mhos or 0.02%. Finally, Longworth (6) quotes a  $\Lambda_0$  value of 149.90 mhos for ammonium chloride at 25° C. We found 149.93 mhos, a difference of 0.02%. It seems, therefore, that we may reasonably claim an accuracy of at least 0.05% in our experimental work. This claim is further supported by the fact that the difference between the limiting conductances of ammonium bromide and ammonium chloride, as determined by us, is equal, within 0.03%, to the difference between the literature values of the limiting conductances of the bromide and chloride ions.

For the determination of  $\Lambda_0$ , the plot of  $\Lambda$  against  $\sqrt{c}$  proposed by Kohlrausch (7) is one of the best methods. The main difficulty in applying this method lies in the fact that the conductances of extremely dilute solutions are required (from 0.002 *N* to 0.0001 *N*) and these are difficult to measure accurately. An alternative method for the evaluation of  $\Lambda_0$  was suggested by Shedlovsky (5). If the function  $\Lambda_0' = (\Lambda + \alpha\sqrt{c})/(1 - \beta\sqrt{c})$ , where  $\alpha$  and  $\beta$  are the Debye-Hückel constants, is plotted against  $c$ , the concentration, a straight line is obtained. The correct value of  $\Lambda_0$  is then derived by extrapolating to zero concentration. Some exceptions to the Shedlovsky rule, however, have been observed. Thus, the function  $\Lambda_0'$  for the alkali nitrates and iodates and silver nitrate passes through a minimum at a concentration of about 0.005 *N*; this vitiates the use of the function for the determination of  $\Lambda_0$  for these salts and the Kohlrausch method must be employed. The chief advantage of the Shedlovsky method lies in its applicability to a far wider concentration range than the Kohlrausch method. Whereas the latter is limited to an upper concentration of 0.002 *N*, the former holds up to 0.1 *N*. Thus, not only does the Shedlovsky method provide a wider working range but it also enhances the accuracy of determination of  $\Lambda_0$ , since measurements at higher concentrations are less subject to error than those at lower concentrations.

The three salts investigated (ammonium bromide, ammonium chloride, and ammonium nitrate) are hydrolyzed in aqueous solution. It was therefore necessary to apply a so-called hydrolysis correction to the experimentally determined equivalent conductances. Since the essence of the hydrolysis of ammonium ion is the replacement of ammonium ions by hydrogen ions, the conductance of the solution is increased and the increase will be the more significant the more dilute the solution. There may be some difference of opinion as to what constitutes the limiting equivalent conductance of a hydrolyzable salt but we define it as the limiting equivalent conductance derived from equivalent conductance measurements which have been corrected for hydrolysis.

The hydrolysis correction may be determined by two different methods. One method, which has been employed by McInnes and Shedlovsky (8) in their determination of the limiting conductance of the acetate ion, consists in measuring the conductance and pH

of a buffered solution. The second method, used in this work, consists in calculating  $x$ , the degree of hydrolysis, from the known value of the hydrolysis constant, i.e.,

$$x = -K_h/2c + \sqrt{[(K_h^2/4c^2) + (K_h/c)]}, \quad [2]$$

where  $K_h$  is the hydrolysis constant and  $c$  the stoichiometric concentration of the salt before hydrolysis. From  $x$ , the "true" conductance of the solution may be calculated as follows: the conductance of 1 g-equiv. of a hydrolyzed salt is made up of the conductance of  $(1-x)$  equivalents of unhydrolyzed salt and  $x$  equivalents of free acid, i.e.,

$$\Lambda = (1-x)\Lambda_{\text{corr}} + x\Lambda_{\text{c}_{\text{HA}}}. \quad [3]$$

In this equation,  $\Lambda$  is the observed equivalent conductance of the solution,  $\Lambda_{\text{corr}}$  is the "true" equivalent conductance of the unhydrolyzed salt, and  $\Lambda_{\text{c}_{\text{HA}}}$  is the equivalent conductance of the free acid in the salt solution. From equation [3] the "true" equivalent conductance of the unhydrolyzed salt follows as

$$\Lambda_{\text{corr}} = (\Lambda - x\Lambda_{\text{c}_{\text{HA}}})/(1-x). \quad [4]$$

$\Lambda_{\text{c}_{\text{HA}}}$  is assumed to be equal to the limiting conductance of the free acid.

The value of  $K_h$ , the hydrolysis constant, was calculated by means of the following formula, due to Bates and Pinching (9):

$$-\log K_h = A_1/T - A_2 + A_3T. \quad [5]$$

From the given values of the constants  $A_1$ ,  $A_2$ , and  $A_3$  and by inserting the appropriate value of  $T$ , viz. 308.16° K., the value of  $K_h$  for ammonium ion at 35.00° C. was found to be  $1.012 \times 10^{-9}$ . The values of  $\Lambda_0$  for hydrochloric and hydrobromic acids were obtained from the literature (10, 11), while that of nitric acid was obtained by adding the limiting conductance of the nitrate ion, as determined by us, to the value of the limiting conductance of the hydrogen ion.

In Table II are summarized the degrees of hydrolysis and the observed and corrected equivalent conductances for the aqueous solutions of the three salts investigated. Also incorporated in this table are the values of the Shedlovsky function  $\Lambda_0'$  derived from the observed and from the corrected equivalent conductances.

The limiting conductances,  $\Lambda_0$ , of the three salts were determined by using both methods of extrapolation described above, and employing observed and corrected equivalent conductances in each case. It was observed that the function  $\Lambda_0'$  obtained from uncorrected equivalent conductance data passed through a minimum but, when corrected equivalent conductances were used, the minimum disappeared. It is our opinion that the increase in  $\Lambda_0'$  with increase in dilution observed in the low concentration region when uncorrected values are used is (in these cases) a direct consequence of hydrolysis. We also believe that the Shedlovsky method for the evaluation of  $\Lambda_0$  is applicable to all three salts investigated, provided the hydrolysis effect is taken into account.

The values of the limiting equivalent conductances for the three salts at 35° C., derived from the application of the Shedlovsky extrapolation method to the corrected equivalent conductances, as well as the mean deviation of the function  $\Lambda_0'$  from the straight line obtained by the method of least squares, are summarized in Table III.

Application of the Kohlrausch method to observed and corrected equivalent conductances resulted in a straight plot in every case. The mean deviations from the straight line obtained by the method of least squares and the respective limiting conductances at 35° C. are summarized in Table IV. It will be observed that  $\Lambda_0$  (uncorrected) is appreciably greater than  $\Lambda_0$  (corrected) and this is undoubtedly due to hydrolysis.

TABLE II  
CONCENTRATIONS, DEGREES OF HYDROLYSIS, OBSERVED AND CORRECTED EQUIVALENT CONDUCTANCES,  
AND UNCORRECTED AND CORRECTED VALUES OF AQUEOUS SOLUTIONS

Concentration, moles/liter $\times 100$	Degree of hydrolysis $\times 10^4$	Observed equivalent conductance, mhos	Corrected equivalent conductance, mhos	Uncorrected $\Lambda_0'$	Corrected $\Lambda_0'$
A. Ammonium chloride					
8.4588	1.0937	155.88	155.87	190.66	190.65
6.6522	1.2333	157.92	157.88	188.65	188.60
5.0333	1.4178	160.06	160.02	186.69	186.64
4.3262	1.5294	161.24	161.19	185.88	185.83
3.8014	1.6315	162.27	162.22	185.34	185.29
3.2216	1.7722	163.44	163.38	184.66	184.59
1.7050	2.4359	167.42	167.34	182.80	182.71
0.18328	7.4180	176.52	176.29	181.54	181.31
0.12245	9.0869	177.23	176.95	181.37	181.06
0.08664	10.8017	177.88	177.54	181.30	180.99
0.07904	11.3089	178.15	177.80	181.45	181.10
0.04769	14.5663	178.85	178.40	181.23	180.96
0.04344	15.2523	179.15	178.67	181.59	181.11
B. Ammonium nitrate					
7.7601	1.1419	149.28	149.24	182.06	181.99
6.1204	1.2857	151.40	151.36	180.40	180.35
5.0620	1.4138	152.98	152.93	179.28	179.23
4.4589	1.5064	154.01	153.96	178.68	178.62
3.6873	1.6566	155.49	155.44	177.88	177.83
3.0658	1.8168	156.82	156.76	177.21	177.15
2.3010	2.0970	158.91	158.84	176.55	176.49
0.46208	4.6787	166.92	166.77	174.79	174.64
0.21946	6.7884	169.32	169.10	174.75	174.51
0.12959	8.8329	170.50	170.22	174.67	174.38
0.10578	9.7762	170.95	170.65	174.72	174.41
0.060330	12.9433	171.86	171.46	174.72	174.30
0.058302	13.1663	171.97	171.56	174.76	174.35
0.050534	14.1413	172.02	171.58	174.62	174.18
0.025730	19.8124	172.92	172.30	174.77	174.15
C. Ammonium bromide					
7.1797	1.1872	159.72	159.68	191.84	191.79
6.3503	1.2623	160.70	160.66	190.84	190.80
4.8576	1.4433	162.73	162.68	189.00	188.95
4.3820	1.5196	163.47	163.42	188.39	188.34
3.7305	1.6469	164.58	164.53	187.53	187.48
2.2073	2.1410	168.04	167.98	185.64	185.57
1.9430	2.2819	168.82	168.75	185.32	185.24
0.26811	6.1418	177.22	177.03	183.33	183.13
0.17723	7.5537	178.24	178.00	183.20	182.96
0.17037	7.7042	178.33	178.09	183.19	182.95
0.096063	10.2586	179.46	179.14	183.11	182.79
0.085742	10.8582	179.74	179.40	183.19	182.85
0.065003	12.4696	180.18	179.79	183.18	182.79
0.036822	16.5645	180.94	180.43	183.20	182.69
0.025495	19.9037	181.51	180.89	183.39	182.77

TABLE III  
LIMITING EQUIVALENT CONDUCTANCES DERIVED BY THE  
SHEDLOVSKY METHOD

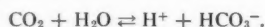
Salt	$\Lambda_0$	Mean deviation of $\Lambda_0'$
Ammonium chloride	180.97	0.03%
Ammonium bromide	182.73	0.02%
Ammonium nitrate	174.21	0.02%



TABLE IV  
 LIMITING EQUIVALENT CONDUCTANCES DERIVED BY THE KOHLRAUSCH METHOD

Salt	Mean deviation		$\Lambda_0$ , mhos	
	Corr.	Uncorr.	Corr.	Uncorr.
Ammonium chloride	0.04%	0.04%	180.86	181.47
Ammonium bromide	0.03%	0.03%	182.57	183.34
Ammonium nitrate	0.02%	0.02%	173.99	174.73

A comparison of the corrected  $\Lambda_0$ 's obtained by the two methods of extrapolation shows that the  $\Lambda_0$  determinations by the Kohlrausch method are in all cases smaller than those by the Shedlovsky method. This discrepancy, amounting to about 0.1%, we believe to be due to a partial "over-correction" of the conductances in the very dilute region. Since the Kohlrausch method depends solely on conductance measurements made in the dilute region it is to be expected that  $\Lambda_0$  derived by this method will be more affected by "over-correction" and therefore will be somewhat lower than the  $\Lambda_0$  derived by the Shedlovsky method, which applies to a much wider concentration range. We believe that the over-correction has resulted from the use of too large a solvent correction for the measured specific conductances of the more dilute solutions. The magnitude of the solvent correction is determined by measuring the conductance of the solvent. The solvent used in this research was water saturated with carbon dioxide under its partial pressure in the laboratory atmosphere. The increase in conductance imparted to the water is due to the ionization of dissolved carbon dioxide:



The equation indicates that the ionization (and therefore the conductance of the carbon dioxide) is repressed by hydrogen ions. In dilute solutions, however, hydrogen ions are produced by hydrolysis. Therefore the ionization of the dissolved carbon dioxide is less in the salt solutions than in pure solvent and hence the magnitude of the solvent correction should be less for these solutions than that determined by measuring the conductance of the pure solvent. Since, however, it was impossible to ascertain quantitatively the extent of the decrease in the magnitude of the solvent correction, the full solvent correction had to be applied.

The limiting equivalent conductance of the ammonium ion at 35.00° C. was determined to be 88.73 mhos  $\pm 0.05$  mho. This represents the average of the two values obtained by subtracting the limiting conductances of the bromide and chloride ions, as determined by Gordon (4), from the limiting conductances of ammonium bromide and ammonium chloride respectively. The limiting conductance of the nitrate ion was then obtained from the limiting conductance of ammonium nitrate. The value thus obtained for nitrate ion at 35.00° C. was 85.48 mhos  $\pm 0.05$  mho.

It is customary, in the work proceeding from this laboratory, to compare experimental results with the conductances calculated by the equations of Falkenhagen and Leist (2) and of Wishaw and Stokes (1), viz.:

$$\Lambda = \Lambda_0 - \frac{e^2}{3DkT} \cdot \frac{\kappa \Lambda_0}{1 + \kappa a} \cdot \frac{q}{(1 + \sqrt{q})(1 + \kappa a \sqrt{q})} - \frac{\eta e^2 1000 \kappa}{3\pi c 9(1 + \kappa a) 10^{11}} \quad (\text{Falkenhagen and Leist}),$$

where the symbols have their usual significance and  $q = \frac{1}{2}$ , and

$$\Lambda = \left( \Lambda_0 - \frac{B_2 \sqrt{c}}{1 + B_2 \sqrt{c}} \right) \left( 1 - \frac{B_1 \sqrt{c}}{1 + B_1 \sqrt{c}} \times F \right) \quad (\text{Wishaw and Stokes}),$$



where  $B_1 = 8.20 \times 10^5 / (DT)^{3/2}$ ,  $B_2 = 82.5 / \eta (DT)^{1/2}$ ,  $B\bar{a}\sqrt{c} = 50.29\bar{a}\sqrt{c} / (DT)^{1/2}$ ,  
and  $F = (\exp 0.2929 B\bar{a}\sqrt{c} - 1) / 0.2929 B\bar{a}\sqrt{c}$ .

The conductances of concentrated solutions of ammonium nitrate at 35.00° C. have been determined by Campbell, Gray, and Kartzmark (12) and the results compared with the results of the Wishaw-Stokes equation in a separate paper (13), but, at that time, they were unacquainted with the Falkenhagen-Leist equation and with the true value of  $\Delta_0$  for ammonium nitrate at 35.00° C. We have now recalculated with the Wishaw-Stokes equation, using the true value of  $\Delta_0$ , and also we have calculated using the Falkenhagen-Leist equation. Results are given in Table V. The Wishaw-Stokes equation was found to give better agreement with experiment than the Falkenhagen-Leist equations. Moreover, the assumed value of 3.0 Å for  $\bar{a}$ , the distance of closest approach of the ions,

TABLE V  
OBSERVED AND CALCULATED EQUIVALENT CONDUCTANCES OF AMMONIUM NITRATE

Concentration, moles/liter × 100	Observed equivalent conductance, mhos	Corr. observed equivalent conductance, mhos	Calculated equivalent conductance			
			Wishaw-Stokes		Falkenhagen-Leist	
			$\bar{a} = 3.0 \text{ Å}$	$\bar{a} = 3.5 \text{ Å}$	$\bar{a} = 3.0 \text{ Å}$	$\bar{a} = 2.3 \text{ Å}$
1074.9	38.52		36.41	38.89	47.85	40.30
940.86	47.46		46.73	49.86	59.99	50.81
767.05	59.84		61.07	65.09	75.98	64.94
713.18	63.86		65.60	69.77	81.43	69.26
550.65	76.46		79.34	84.32	94.75	82.20
397.49	89.17		92.46	97.46	106.37	93.81
245.04	103.2		105.13	109.95	116.58	105.05
191.04	108.2		110.03	114.94	120.01	109.38
169.40	111.0		112.07	116.42	121.41	111.23
102.34	119.4		119.39	122.93	126.43	118.01
7.7601	149.28	149.24	149.47	150.33	150.52	148.94
6.1204	151.40	151.36	151.73	152.41	152.51	151.21
5.0620	152.98	152.93	153.11	153.91	154.02	152.83
4.4589	154.01	153.96	154.38	154.88	154.98	153.97
3.6873	155.49	155.44	155.83	156.26	156.33	155.47
3.0658	156.82	156.76	157.19	157.57	157.62	156.88
2.3010	158.91	158.84	159.14	159.51	159.47	158.90
0.46208	166.92	166.77	166.84	166.93	166.97	166.83
0.21946	169.32	169.10	169.03	169.07	169.09	169.02
0.12959	170.50	170.22	170.19	170.21	170.22	170.17
0.10578	170.95	170.65	170.57	170.58	170.61	170.56
0.060330	171.86	171.46	171.41	171.45	171.45	171.47
0.058302	171.97	171.56	171.48	171.49	171.50	171.48
0.050534	172.02	171.58	171.66	171.68	171.68	171.66
0.025730	172.92	172.30	172.38	172.38	172.40	172.38

is more reasonable than the 2.3 Å required by the Falkenhagen-Leist equation. Spectroscopic indications (14) that the oxygen atoms in the nitrate ion are coplanar with the nitrogen atom and surround the latter at the corners of an equilateral triangle are well supported by electron diffraction data (15). It is, therefore, not unreasonable to suppose that the distance of closest approach of the ammonium and nitrate ions is somewhat smaller (e.g. 3.0 Å) than the value of 4.0 to 6.0 Å usually encountered with ions known to be spherical, e.g.,  $\text{Li}^+$ ,  $\text{K}^+$ . Even, however, if the nitrate ion is assumed to have spherical shape, the distance of 3.0 Å is still less than the sum of the crystallographic radii of the ammonium ion (1.48 Å) and the calculated radius of the nitrate ion (1.34 Å).

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## (-)-HOMOSTACHYDRINE, A NEW ALKALOID ISOLATED FROM THE SEEDS OF *MEDICAGO SATIVA* L. GRIMM<sup>1</sup>

GERHARD WIEHLER<sup>2</sup> AND LÉO MARION

### ABSTRACT

The seeds of *Medicago sativa* (alfalfa) have previously been shown to contain other bases besides stachydrine. One of these bases has now been isolated and found to be a homologue of stachydrine for which the name homostachydrine is suggested. (-)-Homostachydrine is shown to be identical with the (-)-methyl betaine of pipecolic acid. The synthetic racemate of the betaine of pipecolic acid has similar properties to homostachydrine, and their infrared spectra and X-ray powder diagrams are identical.

In the course of a recent study of the biogenesis of stachydrine in *Medicago sativa* L. Grimm (alfalfa), Leete, Marion, and Spenser (1) observed the presence of three unknown bases. Paper chromatography has now revealed that one of these unknown bases accompanies stachydrine through all stages of its isolation from the plant. Chromatography of the reineckates of stachydrine and this unknown base over alumina or of the bases themselves on ion-exchange resins failed to effect any separation. This behavior indicates that the new base is probably closely related to stachydrine. In the course of further experiments on the biogenesis of stachydrine, it became obvious that neither Steenbock (2), who first showed the presence of stachydrine in alfalfa, nor any of the later investigators (3) were dealing with pure stachydrine, but with a mixture.

Since our biogenetic studies with alfalfa involved feeding substances labelled with C<sup>14</sup> to the growing plant and resulted in the formation of radioactive stachydrine (4), it was deemed necessary to separate the unknown base from the stachydrine and to study its structure.

Originally it had been assumed that the unknown base might be betonicine or turicine (1), but this assumption had to be abandoned, since neither of these methyl betaines of hydroxyproline<sup>3</sup> produced a purple spot with Dragendorff's reagent on a paper chromatogram, whereas the unknown base did, and since a hydroxyl base should separate readily from stachydrine on an alumina column.

The unknown base was more abundant in the seeds than in the leaves of alfalfa, and therefore a mixture of the unknown base and stachydrine was isolated from the seeds by a slight modification of the known procedure (1). The crystalline colorless mixture of the hydrochlorides of the bases (m.p. 212–214° decomp.) dissolved in Munier's Bc 20 solvent<sup>4</sup> (5) was chromatographed on a column of cellulose powder and eluted with the same solvent. In this solvent system the unknown base showed a higher  $R_F$  value than stachydrine and was eluted first. The first fractions of the eluate yielded the analytically pure hydrochloride of the new base (m.p. 216–217° decomp.) while the following fractions contained a mixture of the hydrochlorides of the new base and stachydrine. The new base hydrochloride yielded analytical figures corresponding to the empirical formula C<sub>8</sub>H<sub>15</sub>O<sub>2</sub>N.HCl, which is that of a homologue of stachydrine hydrochloride (C<sub>7</sub>H<sub>13</sub>O<sub>2</sub>N.HCl), and it is proposed to designate it homostachydrine.

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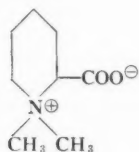
<sup>2</sup>National Research Council of Canada Postdoctoral Fellow 1956–1957.

<sup>3</sup>Samples of betonicine and turicine were given to us by Dr. B. Witkop, National Institute of Health, Bethesda, Maryland, to whom we are most grateful.

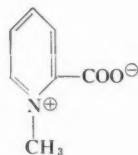
<sup>4</sup>Consists of a mixture of *n*-butanol, concentrated hydrochloric acid, and water, in the proportions of 100 ml.: 20 ml.: 39 ml. respectively.

The specific optical rotation of homostachydrine hydrochloride in absolute ethanol was  $[\alpha]_D -13.3^\circ$  while that of pure stachydrine hydrochloride in the same solvent was  $[\alpha]_D -22.2^\circ$ . Stachydrine isolated from *Galeopsis grandiflora* Lam. (6) and *Citrus aurantium* Amar. (6) appears, from the rotations reported for the hydrochloride, to have been pure since these were in agreement with the rotation of synthetic (-)-stachydrine hydrochloride (7). Steenbock (2), who first isolated stachydrine from alfalfa, reports  $[\alpha]_D -20.7^\circ$  in water, which is appreciably lower than the rotation of synthetic (-)-stachydrine hydrochloride ( $[\alpha]_D -26.7^\circ$  in water) (7). Since stachydrine isolated from alfalfa is always contaminated with homostachydrine, the low rotation reported by Steenbock was probably not due to racemization as he thought, but to the lower rotation of the homostachydrine, which must have been present because his method of isolation would not have separated the two bases.

Although there existed many possible structures for a homologue of stachydrine, it was thought that one of the most likely structures of homostachydrine would be that of the methyl betaine of pipecolic acid (I). Because of the small quantity of homostachydrine available no degradative experiments were tried, but a synthetic specimen of the



I



II

methyl betaine of pipecolic acid was prepared. Following the procedure of Patchett and Witkop (8) for the preparation of betonicine and turicine, the silver salt of ( $\pm$ )-pipecolic acid was converted to the betaine I by treatment with methyl iodide.

The synthetic ( $\pm$ )-betaine hydrochloride, m.p.  $210-211^\circ$  (decomp.), had the same properties as homostachydrine. On a paper chromatogram it showed the same red-purple spot with Dragendorff's reagent and, within the limits of error, the same  $R_F$  value. The infrared spectrum and the X-ray diffraction powder diagram of the synthetic racemate hydrochloride were identical in every respect with those of (-)-homostachydrine hydrochloride. There can be no doubt, therefore, that (-)-homostachydrine is identical with the (-)-methyl betaine of pipecolic acid (I). Attempted resolution of the synthetic racemate with *d*- and *l*-tartaric acids and with *d*-camphorsulphonic acid was unsuccessful.

Although this is the first reported occurrence of homostachydrine, pipecolic acid has been found recently in different plants (9). It has been shown that biogenetically pipecolic acid arises from lysine (10, 11, 12). The occurrence of lysine in alfalfa has been reported (3), and it can be presumed to be the precursor of homostachydrine.

Hoppe-Seyler, who first isolated homarine II from the tissues of *Arca noae* (13), mentions the possibility that it might be formed from lysine. He also assumes that ornithine is the precursor of stachydrine and since the latter occurs with homarine in *Arca noae* (13, 14), he concludes that the two bases are likely synthesized by parallel routes. Since from recent work, however, the pyridine ring does not seem to arise from lysine (15), although this amino acid is the precursor of the piperidine ring (15), it appears most improbable that lysine could be the precursor of homarine.

## EXPERIMENTAL

All the melting points determined by us are corrected. The infrared absorption spectra were measured in nujol mulls on a Perkin-Elmer double beam spectrometer model 21B.

*Isolation of the Mixture of Stachydrine and Homostachydrine*

Air-dried alfalfa seeds (1 kg.) were ground in a Wiley mill and boiled with 70% ethanol (2 l.) for 3 hours. The mixture was filtered and the solid residue extracted twice more by boiling with 70% ethanol (1.5 l.) for 3 to 4 hours. The yellowish-brown filtrates were combined, diluted with water to a volume of 7 l., and treated with lead acetate in the usual way to remove the proteins.

The lead-free filtrate was evaporated to a brown residue (ca. 100 ml.), which was boiled with two successive 300-ml. portions of absolute ethanol. The combined alcoholic extract was filtered and evaporated to a brown viscous sirup. This sirup was boiled with two successive 200-ml. portions of absolute ethanol, and the combined ethanolic solutions evaporated to dryness. The residue thus obtained was dissolved in water (150 ml.) and the solution adjusted to pH 8 with dilute ammonia. A 5% reinecke salt solution in methanol was added and the mixture stored in a refrigerator for 16 hours. The precipitate was filtered off, 100 ml. of the reinecke salt solution added to the choline-free filtrate (16), and the liquor acidified with concentrated hydrochloric acid (50 ml.). A pink crystalline precipitate formed immediately, and after 30 minutes it was filtered with suction and washed with *n*-propanol, the yield of crude reineckate being 4.14 g. This crude reineckate was dissolved in acetone (200 ml.), the solution was filtered to remove some insoluble impurity and evaporated to dryness. The residue (3.87 g.) left after evaporation was dissolved in acetone (250 ml.) and the reineckate converted to the chlorides of the bases by the usual method (17) of treatment with aqueous solutions of silver sulphate (1.56 g.) and barium chloride (1.22 g.). The final filtrate obtained was evaporated to dryness. A crystalline residue resulted, which was extracted with hot absolute ethanol (25 ml.), filtered, and the filtrate evaporated to dryness. This process was repeated twice. The final filtrate was evaporated to dryness, the residue (1.28 g.) was dissolved in water (20 ml.), and the betaines precipitated with mercuric chloride (in 20% hydrochloric acid solution). The mercuric salt complex was filtered with suction, washed with the reagent solution, and decomposed with hydrogen sulphide. After filtration, the solution was evaporated to dryness *in vacuo* leaving a residue of 1.13 g. of crystalline colorless base hydrochlorides. These were dissolved in absolute ethanol (15 ml.) and precipitated by the addition of acetone (200 ml.) and ether (300 ml.). The filtered dry precipitate (0.63 g.) consisted of the pure mixture of stachydrine and homostachydrine hydrochlorides, m.p. 212–214° (decomp.).

A paper chromatogram on Whatman No. 1 paper ascending in Munier's Bc 20 solvent (5) showed two red-purple spots after spraying with a modified Dragendorff's reagent (18),  $R_F$  0.48 (stachydrine) and  $R_F$  0.57 (homostachydrine). The specific optical rotation of the mixture is  $[\alpha]_D^{26} -15.5^\circ$  ( $c$ , 1.55 in absolute ethanol).

*Separation of Homostachydrine from Stachydrine*

"Whatman Standard Grade" ash-free cellulose powder (200 g.) was packed dry into a column, 34 mm. by 530 mm. (19). The column was moistened with Munier's Bc 20 solvent, and a solution of 8-hydroxyquinoline (1.0 g.) in the same solvent (40 ml.) was percolated through the column. It was washed with the solvent for 48 hours, after which it was free of 8-hydroxyquinoline (no color with ferric chloride).



A methanolic solution of 500 mg. of the homostachydrine-stachydrine hydrochlorides was mixed with 10 g. of cellulose powder and dried *in vacuo*. The mixture was then ground in a mortar and conditioned by being kept for some time in an atmosphere of Munier's Bc 20 solvent. In order to indicate the position of the moving solvent front a few drops of a solution of "Orange II" (sodium salt of *p*-(2-hydroxy)-naphthylazo)-benzenesulphonic acid) were added to the top of the column. The conditioned cellulose powder containing the bases was then introduced on top of the wet cellulose column, packed carefully, and moistened with the solvent. The chromatogram was developed by passing Munier's Bc 20 solvent through the column at a rate of flow of 12 ml. per hour. The "Orange II" band reached the outlet of the column after 19 hours, and fractions of 4 ml. were collected by means of an automatic fraction collector. Altogether, 62 fractions were taken, and every fraction was tested by spotting a small amount of the eluate on a filter and spraying with Dragendorff's reagent.

Fraction 38 and all the following ones showed red-purple spots, and chromatography on Whatman No. 1 paper indicated that fractions 38-54 contained homostachydrine exclusively while the later fractions contained both homostachydrine and stachydrine. Fractions 20-54 were pooled and evaporated *in vacuo* to a volume of a few milliliters, water was added, and the evaporation *in vacuo* repeated. The residual yellow liquid was filtered and treated with mercuric chloride as already described above. The homostachydrine hydrochloride obtained after this treatment was crystallized twice from ethanol-ether. It consisted of colorless micropisms, wt. 61 mg., m.p. 216-217° (decomp.),  $[\alpha]_D^{26} - 13.3^\circ$  (c, 1.43 in absolute ethanol). Found: C, 49.61; H, 8.33; N, 7.23; Cl, 18.31. Calc. for  $C_8H_{16}O_2NCl$ : C, 49.37; H, 8.21; N, 7.45; Cl, 18.29%.

The solubility of homostachydrine hydrochloride is very similar to that of stachydrine hydrochloride. Both salts are readily soluble in water and alcohol, slightly soluble in acetone, and insoluble in ether, petroleum ether, and carbon tetrachloride.

#### *Synthesis of (±)-Methylbetaine of Pipecolic Acid*

$\alpha$ -Picoline (50 g.) was oxidized with potassium permanganate (20) to  $\alpha$ -picolinic acid, which was isolated as the hydrochloride (34 g.), m.p. 213-216° (decomp.). The  $\alpha$ -picolinic acid hydrochloride in water was hydrogenated over platinum oxide catalyst as described by Stevens and Ellman (21). The crystalline product, after recrystallization from alcohol-benzene and methanol-acetone, consisted of 19.27 g. of pure (±)-pipecolic acid hydrochloride, m.p. 259-262° (decomp.). (±)-Pipecolic acid hydrochloride (2.58 g., 0.0156 mole) was dissolved in water (6 ml.) and, according to the procedure of Patchett and Witkop (8), silver oxide (6.95 g., 0.03 mole) was added to the solution. After 4 hours, water (4 ml.) was removed by distillation *in vacuo* and methanol (50 ml.) and methyl iodide (3.8 ml., 0.061 mole) were added to the residual mixture, which was warmed gently for a few minutes and then kept at room temperature for 1 hour. Another 3.8 ml. of methyl iodide was added, the mixture refluxed for 2.5 hours, and the precipitate filtered and washed with methanol. The combined filtrate and washings were evaporated *in vacuo* leaving the free base as an hygroscopic oil which was dissolved in absolute ethanol (50 ml.). Hydrogen chloride was passed through the solution, which was subsequently evaporated *in vacuo*. The crystalline residue was dissolved in absolute ethanol, the solution treated with charcoal and filtered, and the filtrate mixed with acetone. (±)-Pipecolic acid methylbetaine hydrochloride crystallized out (1.30 g., 0.0067 mole; yield, 43%), m.p. 208-209° (decomp.). A second crystallization from alcohol-acetone yielded 0.90 g. of the pure hydrochloride, m.p. 210-211° (decomp.). Found: C, 49.71; H, 8.44; N, 7.21. Calc. for  $C_8H_{16}O_2NCl$ : C, 49.61; H, 8.33; N, 7.23%.



A chromatogram on Whatman No. 1 paper developed with Munier's Bc 20 solvent showed a red-purple spot ( $R_F$  0.56–0.58) after a spray with Dragendorff's reagent. Under the same conditions (–)-homostachydrine hydrochloride showed a red-purple spot at the same  $R_F$  value. The infrared absorption spectra in nujol mulls of both the synthetic hydrochloride and (–)-homostachydrine hydrochloride were identical in every respect, and showed a strong carbonyl absorption band at  $1705\text{ cm}^{-1}$ . The X-ray powder patterns were also identical.

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# THE PHOTOLYSIS OF AZOETHANE<sup>1</sup>

H. CERFONTAIN<sup>2</sup> AND K. O. KUTSCHKE

## ABSTRACT

The photolysis of azoethane at  $\lambda$  3660 Å has been reinvestigated. The quantum yield of nitrogen formation was found to be dependent on the azoethane pressure and the temperature, indicating collisional deactivation of excited azoethane molecules.

The results confirm the mechanism proposed by Ausloos and Steacie (1). For the activation energy of the addition reaction  $C_2H_5 + C_2H_5N_2C_2H_5$  a value of  $6.0 \pm 0.3$  kcal./mole has been obtained, assuming a negligible activation energy for the combination reaction of two ethyl radicals.

## INTRODUCTION

The formation of nitrogen in the photooxidation of azoethane (2) was found to be greater than expected and dependent on the pressures of azoethane and oxygen, as well as on the temperature.

Weininger and Rice (3) have studied the primary process in the photolysis of azoethane and showed that the quantum yield of nitrogen formation was dependent on the azoethane pressure in a manner which is explicable in terms of an activated molecule intermediate. In their study they made the implicit assumption that the quantum yield was independent of temperature. On the other hand, Durham and Steacie (4) found the quantum yield of nitrogen formation in the photolysis of azoisopropane to be temperature dependent. This suggested that a reinvestigation of the primary process in the photolysis of azoethane would be required in order to be certain of temperature effects for the photooxidation studies.

## EXPERIMENTAL

Azoethane was obtained from Merck and Company. It was distilled several times and stored behind a mercury cutoff in a blackened tube. The reaction cell, with a volume of 180 ml., was completely filled with a parallel beam of light. The total reaction cell system, including a cold finger, a magnetically driven stirrer, and connecting tubing, had a volume of 282 ml. The analytical section consisted of a solid nitrogen trap, two Ward stills, a McLeod gauge, a diffusion pump, and a combined Toepler pump and gas burette. The photolysis products were separated as follows: Nitrogen was removed at solid nitrogen temperature;  $C_2$  hydrocarbons were separated at  $-165^\circ$  C. and analyzed mass spectrometrically. Butane was removed at  $-125^\circ$  C.

A Hanovia S 500 medium pressure mercury arc was used as a light source, together with a Corning filter 5860 which limited the effective radiation to the 3660 Å group of lines. Absorption measurements were made with a photocell coupled to a sensitive galvanometer. At low azoethane concentrations ( $<0.001$  mole/l.) the absorption measurements suffered from lack of precision. In this case the light absorption was calculated from the extinction coefficient, which was estimated from the experiments at higher concentration. For the highest concentration used, about 75% of the light was absorbed. Quantum yield measurements were carried out using a potassium ferrioxalate actinometer (5, 6) according to the procedure modified by Baxendale (5). The experiments were done at room temperature in subdued light. The radiation was completely absorbed by the actinometer. For these conditions, Hatchard and Parker (6) report a quantum yield of 1.21 for the actinometer at  $\lambda$  3660 Å.

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<sup>2</sup>N.R.L. Postdoctorate Fellow 1955-57.

## RESULTS AND DISCUSSION

*Primary Processes*

The light intensity was measured by placing the actinometer cell before and after the reaction cell. In the first position the intensity was found to be  $1.64 \times 10^{16}$  and  $1.70 \times 10^{16}$  quanta/second; in the second position  $1.16 \times 10^{16}$  and  $1.00 \times 10^{16}$  quanta/second. This observed difference appreciably exceeds that accounted for by simple reflections only. Assuming identical absorption and scattering by the front and rear windows of the reaction cell to be the only cause of light loss, a transparency factor  $\alpha = 0.85^\dagger$  per window was calculated from these data. Corrections for this and for first-order reflections from quartz-gas and pyrex-gas interfaces were made for all measurements, applying the general argument of Farkas and Melville (8) to our optical system. The data for the dependence of the nitrogen formation on temperature and azoethane concentration are given in Table I. The molar extinction coefficient  $E$  was calculated

TABLE I  
EFFECT OF TEMPERATURE AND PRESSURE ON QUANTUM YIELD

Temp., ° C.	Azoethane conc., mole l. <sup>-1</sup> $\times 10^3$	$I_a$ , quanta second <sup>-1</sup> $\times 10^{-16}$	$R_{N_2}$ , molec. second <sup>-1</sup> $\times 10^{-16}$	$1/\phi$	$E$ , l. mole <sup>-1</sup> cm. <sup>-1</sup>
28	7.16	1.10	0.648	1.70	19.1
	5.08	0.93	0.608	1.53	19.3
	3.57	0.75	0.533	1.41	19.0
	2.20	0.53	0.403	1.32	19.5
	1.45	0.380	0.305	1.24	19.5
	0.68	0.202	0.172	1.17	
78	6.75	1.10	0.710	1.55	19.5
	4.53	0.91	0.630	1.43	20.2
	2.90	0.68	0.527	1.28	20.2
	1.74	0.449	0.378	1.19	19.3
	0.83	0.248	0.216	1.15	
116	6.48	1.01	0.735	1.38	20.2
	4.16	0.79	0.619	1.27	20.6
	2.76	0.59	0.495	1.18	19.6
	1.80	0.431	0.374	1.15	20.8
	0.64	0.185	0.167	1.11	
152	6.16	1.07	0.915	1.17	20.4
	3.86	0.82	0.736	1.11	20.4
	1.91	0.490	0.436	1.12	20.5
	1.48	0.402	0.390	1.03	20.8
	0.68	0.206	0.207	1.00	

from  $\ln I/I_0 = -Ecd$ . Fig. 1 shows the relation between the quantum yield of nitrogen formation, temperature, and pressure. The accuracy of the actinometer measurements is  $\pm 10\%$ . This means that the uncertainty in the  $1/\phi$  scale is  $\pm 10\%$ . It should be recognized, however, that the uncertainty in the  $1/\phi$  values relative to each other is much less than this.

The mechanism proposed by Weininger and Rice (3) represents the results satisfactorily:



$^\dagger$ This  $\alpha$  corresponds to  $1-A$  of Hunt and Hill (7).

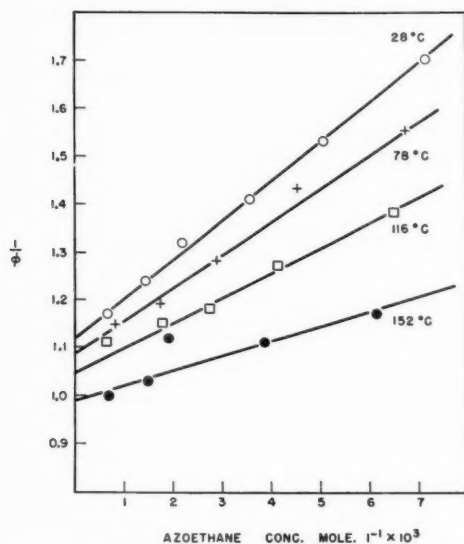


FIG. 1. Effect of pressure on reciprocal quantum yield of nitrogen formation from azoethane.

where  $A^*$  represents an excited azoethane molecule. From a steady state treatment of the excited azoethane molecules, the following relation may be deduced:

$$1/\phi = 1 + (k_3/k_2) |A|, \quad [4]$$

where  $\phi$  represents the quantum yield of nitrogen formation and  $|A|$  the azoethane concentration.

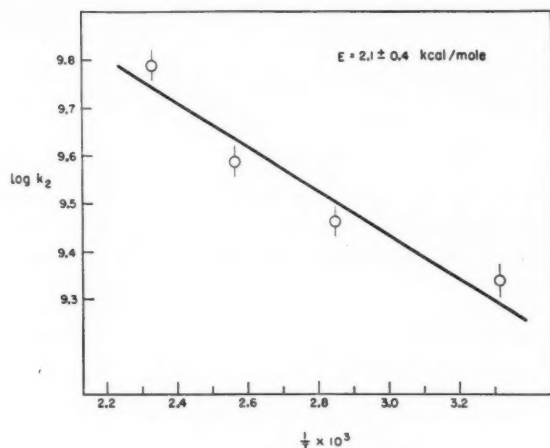
It follows from relation [4] that a plot of  $1/\phi$  against  $|A|$  should be linear at each temperature with an intercept of unity, in close agreement with the experiments. By determining the slopes of these lines, values for  $k_3/k_2$  at each temperature were derived.

The rate constant for deactivation  $k_3$  was calculated from collision theory assuming zero activation energy and a steric factor of unity. A value of  $7.0 \text{ \AA}$  was assumed for the kinetic collision diameters of normal and excited azoethane molecules. As shown in Table II,  $k_2$  is temperature dependent. An Arrhenius plot (Fig. 2) shows the activation energy  $E_2$  to be  $2.1 \pm 0.4 \text{ kcal./mole}$ .

TABLE II  
VALUES OF RATE CONSTANTS

Temp., °C.	$k_3$ , molec. <sup>-1</sup> cm. <sup>3</sup> second <sup>-1</sup> $\times 10^{10}$	$k_3/k_2$ , molec. <sup>-1</sup> cm. <sup>3</sup> $\times 10^{19}$	$k_2$ , second <sup>-1</sup> $\times 10^{-9}$
28	2.96	1.35	2.19
78	3.20	1.13	2.84
116	3.37	0.88	3.84
152	3.52	0.515	6.8

The following observations indicate that the mechanism mentioned above is oversimplified:

FIG. 2. Arrhenius plot of  $k_2$ .

(a) At higher temperatures nitrogen is formed not only by the primary process, but also by thermal decomposition of the  $C_2H_4N_2C_2H_5$  radical (1),



An estimate of the amount of nitrogen produced by reaction [15] was made as follows: The amount of ethylene formed by disproportionation was calculated from the amount of butane, using a value of 0.12 for the ratio of disproportionation to combination of ethyl radicals (see below, *Secondary Processes*). The deviation of this amount from the total amount of ethylene formed was assumed to be due to reaction [15] only and is consequently equal to the amount of nitrogen formed by this reaction. The percentage of nitrogen formed under our experimental conditions by reaction [15] is 0.8% of the total amount at 107° C. and 2% at 152° C. This effect is very small, even at the highest temperatures employed; hence it can be neglected for the calculation of  $k_2$ .

(b) The intercepts of the reciprocal quantum yields of nitrogen show a small increase with a decrease in temperature.

(c) The curvature of the Arrhenius plot for  $k_2$  probably exceeds experimental error.

(d) A fluorescence spectrogram did not indicate any fluorescence.

All these facts might well be explained by a diffusion controlled deactivation reaction of excited molecules at the wall of the reaction cell,

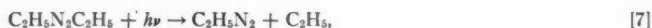


As the rate of disappearance of  $A^*$  varies exponentially with temperature and the rate of diffusion varies with the square root of the temperature, an increasing deviation from unity for the reciprocal quantum yield at zero pressure may be expected with decreasing temperature. The rate of disappearance of excited molecules for wall deactivation is given by  $k|A^*|/|A|$ . From a steady state treatment for excited azoethane molecules one can derive

$$1/\phi = 1 + (k_3/k_2)|A| + (k/k_2)|A|. \quad [6]$$

Applying this equation, a corrected value for  $E_2$  was calculated and found to be  $2.4 \pm 0.4$  kcal./mole.

An alternative explanation might involve the  $C_2H_5N_2$  radical, which might recombine with ethyl or decompose:



The stability of the  $C_2H_5N_2$  radical is expected to be greatest at low temperatures, and this results in a maximum decrease in quantum yield for the nitrogen formation at these temperatures. The quantum yield of nitrogen formation should be intensity dependent in the temperature range in which the lifetime of the  $C_2H_5N_2$  radical is comparable to the time between collisions of  $C_2H_5$  and  $C_2H_5N_2$  radicals. The observed quantum yield, however, (Table III) is independent of the light intensity. It may therefore be concluded that the lifetime of  $C_2H_5N_2$  is short compared to the time between collisions. Reaction [9] can therefore be excluded.

TABLE III  
EFFECT OF LIGHT INTENSITY ON QUANTUM YIELD AT 28° C.

Azoethane conc., mole l. <sup>-1</sup> × 10 <sup>3</sup>	$I_a$ , quanta second <sup>-1</sup> × 10 <sup>-16</sup>	$R_{N_2}$ , molec. second <sup>-1</sup> × 10 <sup>-16</sup>	1/φ
0.75	0.242	0.215	1.12
0.75	0.0246	0.0212	1.16
0.75	0.00286	0.00248	1.15

Internal conversion of the excited azoethane molecule to another electronic state which is incapable of dissociation (9) might be considered as a third explanation,



From a steady state treatment of excited azoethane molecules it follows that

$$1/\phi = 1 + k_{10}/k_2 + (k_3/k_2)|A|. \quad [11]$$

The value of  $k_2$  increases with increasing temperature (Table II) and if  $k_{10}$  is less temperature dependent, the intercept of the plot of  $1/\phi$  against  $|A|$  may be expected to decrease with increasing temperature, and to approach unity, as is, in fact, the case. Collisional deactivation has been observed in the photolysis of azoisopropane (4). For azomethane (10) the quantum yield of decomposition was found to be unity, independent of temperature and pressure. The difference in collisional deactivation for the three homologous azoalkanes is illustrated in Fig. 3. It is generally accepted (3) that, although the primary excitation in photochemical decompositions is mainly electronic, the mechanism of decomposition involves its transfer to vibrational energy and the accumulation of this energy in a particular bond. Hence the reasonable observation is made that collisional deactivation is negligible in the photolysis of azomethane, but is of considerable importance in the photolysis of the higher homologues because of their larger number of degrees of vibrational freedom.

#### Secondary Processes

The results of the photolysis are shown in Table IV. To avoid side reactions the



TABLE IV  
PHOTOLYSIS OF AZOETHANE

Temp., °C.	Relative intensity	Conc., azo, molec. cm. <sup>-3</sup> × 10 <sup>-13</sup>	Products, molec. cm. <sup>-3</sup> second <sup>-1</sup> × 10 <sup>-13</sup>	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{C_2H_2}$	$R_{C_2H_6} + R_{C_2H_4} + R_{C_2H_2}$	$k_{12}/k_{13}$ , molec. <sup>-1</sup> cm. <sup>3/2</sup> second <sup>-1</sup> × 10 <sup>13</sup>	$R_{T.F.H.}$ , molec. cm. <sup>-3</sup> second <sup>-1</sup> × 10 <sup>-13</sup>	$k_{21}/k_{12}$ , molec. <sup>-1</sup> cm. <sup>3/2</sup> second <sup>-1</sup> × 10 <sup>13</sup>
27	9.7	0.492	0.118	0.0166	0.0114	0.0972	0.118	0.965	0.0041	0.85
30	98	0.326	0.883	0.0972	0.0884	0.772	0.114	0.985	0.013	1.4
28	93	0.605	1.58	0.189	0.166	1.33	0.124	0.961	0.062	2.7
31	90	0.641	1.58	0.176	0.156	1.36	0.116	0.959	0.065	2.7
27	90	0.845	1.97	0.209	0.181	1.63	0.111	0.940	0.118	3.4
29	35	0.627	0.589	0.0750	0.0583	0.500	0.117	0.975	0.015	1.0
78	96	0.497	1.20	0.189	0.110	0.915	0.120	0.925	0.090	4.5
107	88	0.605	1.77	0.413	0.131	1.19	0.110	0.905	0.168	8.0
107	89	0.567	1.66	0.374	0.147	1.14	0.128	0.910	0.149	7.8
107	89	0.507	1.61	0.384	0.143	1.07	0.133	0.902	0.158	9.6
116	88	0.386	0.927	0.218	0.0722	0.628	0.115	0.912	0.082	8.4
118	90	0.381	0.944	0.236	0.0689	0.595	0.116	0.882	0.111	12.0
152	95	0.299	1.05	0.355	0.0761	0.547	0.139	0.861	0.146	20.9
175	89	0.436	1.54	0.833	0.117	0.467	0.250	0.843	0.242	25.8
175	89	0.507	1.82	0.965	0.125	0.500	0.250	0.804	0.356	31.3
175	91	0.555	1.96	1.02	0.141	0.561	0.251	0.813	0.366	27.8

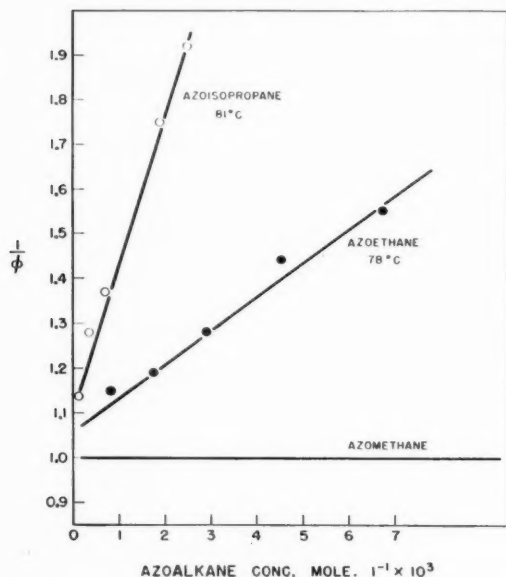
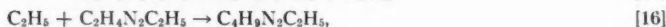
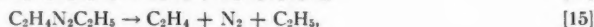
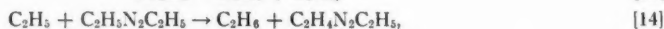


FIG. 3. Effect of pressure on reciprocal quantum yield of nitrogen formation from the lower azoalkanes.

conversion was kept below 3%. Ausloos and Steacie (1) explained their results in the photolysis of azoethane by means of the following mechanism:



Assuming ethylene, ethane, and butane to be formed only by reactions [12], [13], and [14], the following relations should be obeyed:

$$\frac{R_{C_2H_4}}{R_{C_4H_{10}}} = \frac{k_{13}}{k_{12}} \quad [18]$$

$$\frac{R_{C_2H_6} - R_{C_2H_4}}{R_{C_4H_{10}}} = \frac{k_{14}[A]}{k_{12}^{1/2} R_{C_4H_{10}}^{1/2}} \quad [19]$$

$$\frac{R_{C_2H_6} + R_{C_2H_4}}{R_{C_4H_{10}}} = 2 \frac{k_{13}}{k_{12}} + \frac{k_{14}[A]}{k_{12}^{1/2} R_{C_4H_{10}}^{1/2}} \quad [20]$$

The ratio  $R_{C_2H_4}/R_{C_4H_{10}}$  is found to be constant with a value of  $0.12 \pm 0.01$  in the temperature range 27–118°C. This means that  $E_{13} - E_{12} = 0$  (cf. Shepp and Kutschke (11)). At higher temperatures an increase in the ethylene to butane ratio is observed owing to thermal decomposition of  $C_2H_4N_2C_2H_5$ . In Fig. 4,  $(R_{C_2H_6} + R_{C_2H_4})/R_{C_4H_{10}}$  and  $(R_{C_2H_6}$

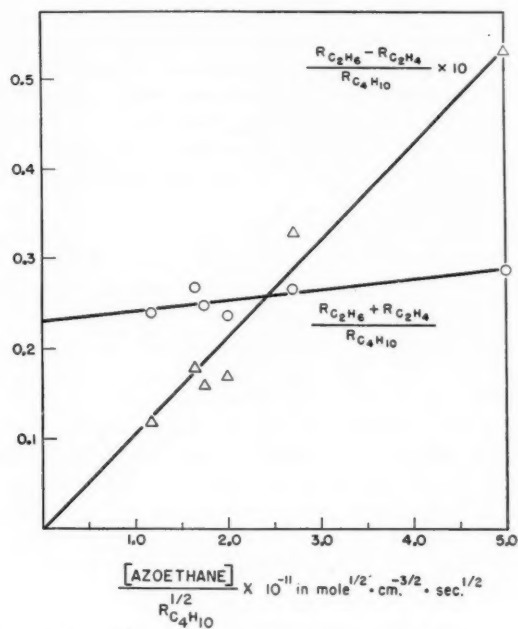


FIG. 4. Plot of  $(R_{C_2H_6} + R_{C_2H_4})/R_{C_4H_{10}}$  and  $(R_{C_2H_6} - R_{C_2H_4})/R_{C_4H_{10}}$  vs.  $[A]/R_{C_4H_{10}}^{1/2}$ .

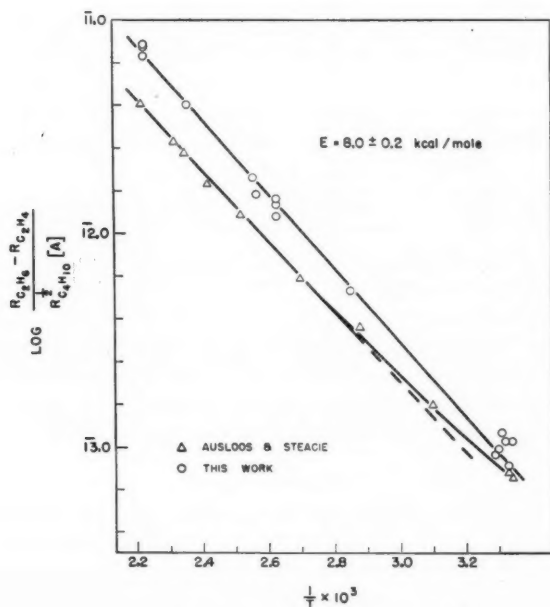
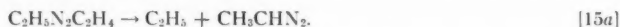


FIG. 5. Arrhenius plot of  $k_{14}/k_{12}^{1/2}$ .

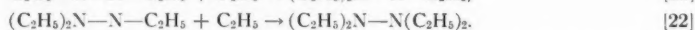
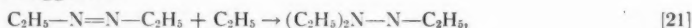
$-R_{C_2H_4}/R_{C_4H_{10}}$  are plotted against  $|A|/R_{C_4H_{10}}^{1/2}$  for runs at 28° C. According to relation [20] the intercept of this curve with the ordinate should be equal to  $2k_{13}/k_{12}$ . A value of  $k_{13}/k_{12} = 0.12 \pm 0.01$  was obtained. Values of  $k_{14}/k_{12}^{1/2}$  were calculated from relation [19]. By plotting  $\log k_{14}/k_{12}^{1/2}$  against  $1/T$  (Fig. 5) a value of  $E_{14} - \frac{1}{2}E_{12} = 8.0 \pm 0.2$  kcal./mole was obtained. This value is higher than that reported by Ausloos and Steacie, who estimated  $E_{14} - \frac{1}{2}E_{12} = 7.5 \pm 0.1$  kcal./mole. This low value, as well as the curvature they observed in the Arrhenius plot below 70° C., may well be explained by a small impurity in their azoethane sample.

Some high (~20%) conversion experiments were done in order to accumulate significant quantities of heavier products for possible mass spectrometric identification; the fraction remaining after butane and higher products were removed was submitted for analysis. After subtraction of the contributions due to unreacted azoethane a large number of peaks remained between masses 28 and 150. In particular the presence of major peaks at masses 114 and 144, together with peaks corresponding to plausible fragments, suggested that ethyl butyl diimide and tetraethyl hydrazine are amongst the products. In addition, peaks at masses 56, 55, and 42, possibly corresponding to the ions  $C_2H_4N_2^+$ ,  $C_2H_3N_2^+$ , and  $C_2H_4N^+$  or  $CH_2N_2^+$  respectively, suggested the presence of diazoethane. These ions might also arise as fragments in the spectrum of ethyl butyl diimide, however, and in the absence of pure standards the identification can be considered tentative only. Should diazoethane be a product, reaction [15a] could be suggested as a source. This is similar to the reaction thought to lead to methyl ketene in the photolysis of diethyl ketone (12),



Since diazoethane is transparent at  $\lambda$  3660 Å (13) no photolysis is expected even under conditions of high conversion.

The material balance  $(R_{C_2H_6} + R_{C_4H_{10}})/R_{N_2}$  should be equal to unity if only reactions [2], [12], [13], [14], [15], and [16] are involved and should be greater than unity if reaction [15a] or [17] occurs as well. As can be seen from Table IV a value smaller than unity was observed, showing a decrease with increase in temperature. Since tetraethyl hydrazine is probably among the products, the following addition reactions between ethyl radicals and azoethane may be suggested:



The rate of formation of tetraethyl hydrazine will be equal to  $R_{T.E.H.} = R_{N_2} - R_{C_4H_{10}} - R_{C_2H_6}$  subject to the following assumptions:

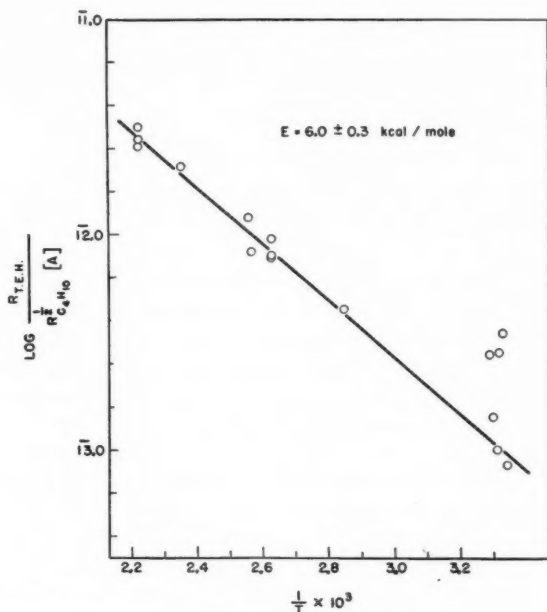
(a) Reaction [21] is the rate determining step in the formation of tetraethyl hydrazine.

(b) Reaction [15], [15a], and [17] may be neglected, i.e., for every molecule of ethane formed by abstraction, a molecule of ethyl butyl diimide is formed. As pointed out before, the number of  $C_2H_5N_2C_2H_4$  radicals disappearing by reaction [15] is small.

The following relation may be deduced on this basis:

$$k_{21}/k_{12}^{1/2} = R_{T.E.H.}/R_{C_4H_{10}}^{1/2}|A|. \quad [23]$$

By plotting  $\log k_{21}/k_{12}^{1/2}$  against  $1/T$  (Fig. 6) a value of  $E_{21} - \frac{1}{2}E_{12} = 6.0 \pm 0.3$  kcal./mole was obtained. A large scatter in  $R_{T.E.H.}$  and  $\log k_{21}/k_{12}^{1/2}$  may be expected at low temperatures since the material balance approaches unity under these conditions. The present value of  $E_{21} - \frac{1}{2}E_{12}$  is in agreement with the activation energies for other reactions of the addition of radicals to double bonds (10, 14, 15).

FIG. 6. Arrhenius plot of  $k_{21}/k_{12}^{1/2}$ .

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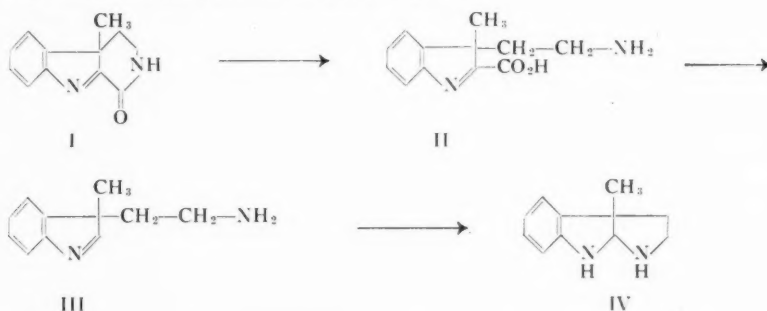
# TRYPTAMINES, CARBOLINES, AND RELATED COMPOUNDS PART IV. ATTEMPTED SYNTHESIS OF THE PHYSOSTIGMINE RING SYSTEM<sup>1,2</sup>

R. A. ABRAMOVITCH<sup>3</sup>

## ABSTRACT

4-Methylpiperid-2,3-dione-3-phenylhydrazone failed to undergo ring closure under Fisher-cyclization conditions but rearranged to a more stable form of the phenylhydrazone. *Cis-trans* isomerism is suggested for the two forms.

In Parts II and III (1, 2) a relatively general method of preparing tryptamines was developed which involved the hydrolysis of 1,2,3,4-tetrahydro-1-oxo- $\beta$ -carbolines to tryptamine-2-carboxylic acids, followed by decarboxylation. It occurred to us that if the tryptamine-2-carboxylic acid had a 3-methyl substituent (II) decarboxylation of this indolenine carboxylic acid would give rise to an amine (III) which should cyclize readily to give the tricyclic system (IV) present in physostigmine.



To this end, ethyl malonate was condensed with allyl cyanide to give diethyl (2-cyano-1-methyl)ethylmalonate (V). Allyl cyanide rearranges in the presence of alkali to crotononitrile, and it is this which undergoes the Michael addition (3). Similar reactions involving the addition of fluorene (4) and 9-monosubstituted fluorenes (5) to crotononitrile following the allylic rearrangement have been reported. The nitrile (V) was catalytically reduced under pressure to give 3-ethoxycarbonyl-4-methyl-2-oxopiperidine (VI), which was hydrolyzed to the corresponding acid. This was not isolated but its solution was treated with benzenediazonium chloride at pH 4, when it underwent the Japp-Klingemann reaction giving the phenylhydrazone (VII). The conditions of the Japp-Klingemann reaction were found, as in previous cases (1, 2), to be critical because at lower or higher pH's considerable tar formation took place.

Cyclization of the phenylhydrazone (VII) to the indolenine (I) could not be effected. Under mild conditions which effect the cyclization of unsubstituted piperidone phenylhydrazones (e.g. boiling with 90% acetic acid) VII was unchanged. If more powerful reagents were used for prolonged periods only tar formation took place. With boron trifluoride in acetic acid, or with zinc chloride, the phenylhydrazone (VII) rearranged to a

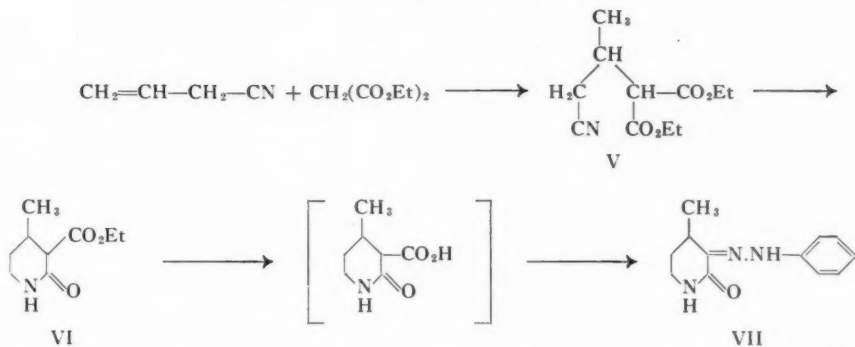
<sup>1</sup>Manuscript received November 6, 1957.

Contribution from King's College, University of London, Strand, London, W.C.2, England.

<sup>2</sup>Part III: *J. Chem. Soc.* 4593 (1956).

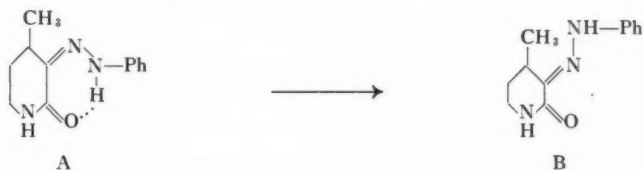
<sup>3</sup>I.C.I. Research Fellow at King's College. Present address: Chemistry Department, University of Saskatchewan, Saskatoon, Sask., Canada.





more stable form which resisted all attempts to effect cyclization. This rearrangement of a phenylhydrazone to a more stable form, instead of undergoing cyclization, is not unique; Snyder and Smith (6) found that ethyl 4-cyano-2-oxobutyrates 2-phenylhydrazone was isomerized to a more stable form but could not be induced to cyclize. The failure of our phenylhydrazone to cyclize is somewhat surprising since Millson and Robinson (7) were able to prepare the tetrahydro-9,11-dimethylcarbazoles from the 2-methylcyclohexanone *N*-methoxyphenyl-*N*-methylhydrazones, so that possible hindrance arising from the conformation of the methyl-group does not seem to be the cause.

It seems probable that the isomerism of these hydrazones is geometrical. Recently, we have obtained evidence for the existence of such geometrical isomerism with the phenylhydrazones of pyruvamide and methyl pyruvate (8), and it had previously been observed with acetaldehyde phenylhydrazone (9) and pyruvic acid 2,4-dinitrophenylhydrazone (10). Consideration of the positions of the amide-carbonyl absorption bands in the infrared spectra of the isomeric phenylhydrazones studied here suggests that the more stable form (B) has the *anti*-configuration while the form (A) obtained from the Japp-Klingemann reaction has the *syn*-configuration.



The difference in the amide C=O frequencies is not, however, as large as in the other cases previously studied so that the assignments are only tentative. The *syn*-form, which has the possibility of being intramolecularly hydrogen bonded, should exhibit a lower  $\nu_{\text{CO}}$  ( $1658 \text{ cm}^{-1}$  in this case) than the *anti*-structure ( $1669 \text{ cm}^{-1}$ ), where this possibility does not exist.

In view of the failure to effect cyclization at this stage the piperidone (VII) was hydrolyzed to the amino acid. This route, however, offers no advantage over well-established approaches to the physostigmine ring system and was, therefore, not pursued further.

#### EXPERIMENTAL

M.p.'s and b.p.'s are uncorrected. Infrared spectra were measured on a Grubb-Parsons model S4 double-beam instrument with sodium chloride optics.

*Diethyl (2-Cyano-1-methyl)ethylmalonate*

Ethyl malonate (16 g.) was added to a cold solution of sodium (0.5 g.) in ethanol (20 ml.). To this solution was added dropwise with stirring a solution of allyl cyanide (4 g.) in absolute ethanol (10 ml.), the temperature being maintained below 35°. The solution was kept at room temperature overnight, treated with acetic acid (1.3 g.), and the alcohol evaporated under reduced pressure. The residue was extracted with ether and the extract dried (MgSO<sub>4</sub>) and evaporated, eventually *in vacuo* at 130° (water pump). The residue was distilled under reduced pressure giving the colorless ester (11.7 g.), b.p. 180° at 16 mm., 119° at 0.4 mm. Calc. for C<sub>11</sub>H<sub>17</sub>O<sub>4</sub>N: C, 58.2; H, 7.5; N, 6.2. Found: C, 58.4; H, 7.7; N, 6.55. I.R. spectrum (liquid film) (main bands only): C≡N, 2283 cm.<sup>-1</sup> (w); (CO<sub>2</sub>Et)<sub>2</sub>, 1742 (s), 1730 cm.<sup>-1</sup> (s).

*3-Ethoxycarbonyl-4-methyl-2-oxopiperidine*

The above malonate (30 g.) in commercial absolute ethanol (120 ml.) was hydrogenated in the presence of Raney nickel (1 g.) at 80° and 100 atm. until hydrogen uptake was complete (*ca.* 3–4 hours). The filtered solution was evaporated, eventually under reduced pressure, on the water bath, and the cooled residue treated with light petroleum (b.p. 60–80°). Crystallization occurred immediately. The product (24 g.) was filtered, washed with cold light petroleum, and recrystallized from that solvent containing a few drops of benzene, giving colorless plates, m.p. 83–84°. Calc. for C<sub>9</sub>H<sub>15</sub>O<sub>3</sub>N: C, 58.4; H, 8.2. Found: C, 58.6; H, 8.1.

*4-Methylpiperid-2,3-dione-3-phenylhydrazone (A)*

3-Ethoxycarbonyl-4-methyl-2-oxopiperidine (1.85 g.) in water (20 ml.) containing potassium hydroxide (0.6 g.) was kept at room temperature for 18 hours. The solution was cooled in ice and treated, with stirring, with a partially neutralized solution (30 ml.) of benzenediazonium chloride prepared from aniline (0.97 g.) and sodium nitrite (0.55 g.), and the pH of the mixture immediately adjusted to *ca.* 4 by addition of glacial acetic acid. Ammonium chloride (4 g.) was added and stirring was continued, the temperature of the solution being slowly allowed to reach room temperature. After 10 hours the solid which had separated was filtered, washed with water, and recrystallized from dilute alcohol giving the phenylhydrazone (A), m.p. 141–142°. Calc. for C<sub>12</sub>H<sub>15</sub>ON<sub>3</sub>: C, 66.3; H, 7.0. Found: C, 66.0; H, 7.0. I.R. spectrum (Nujol mull): NH, 3185 cm.<sup>-1</sup> (broad); CO (amide), 1658 cm.<sup>-1</sup> (s); C<sub>6</sub>H<sub>5</sub>- 751, 702 cm.<sup>-1</sup> (s). The picrate separated from a small volume of alcohol as dark red needles, m.p. 105–106°.

*Attempted Fisher Cyclization of the Phenylhydrazone (A)*

(a) The phenylhydrazone (0.5 g.) in glacial acetic acid (2 ml.) was treated with a 45% ethereal solution (0.36 g.) of boron trifluoride. The solution turned red and the solid complex separated. The suspension was slowly heated to 60°, when the solid went into solution, and this was then boiled for 2 minutes, poured into cold water, and the acid neutralized with an excess of saturated aqueous sodium carbonate solution. The crude yellow product which separated was insoluble in boiling water and only sparingly soluble in boiling ethanol, but readily soluble in hot dilute ethanol, from which it was recrystallized, giving colorless flat needles (0.19 g.) of the phenylhydrazone (B), m.p. 207–208°. Calc. for C<sub>12</sub>H<sub>15</sub>ON<sub>3</sub>: C, 66.3; H, 7.0; N, 19.3. Found: C, 66.1; H, 6.75; N, 18.8. I.R. spectrum (Nujol mull): NH 3226 cm.<sup>-1</sup>; CO (amide) 1669 cm.<sup>-1</sup> (s); C<sub>6</sub>H<sub>5</sub>- 754, 692 cm.<sup>-1</sup> (s). The picrate separated from a small volume of ethanol as yellow needles, m.p. 139–140°. The filtrate from the recrystallization of the crude product was evaporated to a small volume giving crystals of the starting phenylhydrazone (A) (0.22 g.), m.p. 136–138°, un-depressed on admixture with an authentic sample, m.p. 141–142°.

If the acetic acid solution was boiled for  $\frac{1}{2}$  hour instead of 1 minute only a dark brown gum was obtained which could not be purified. Boiling the phenylhydrazone (A) with an absolute ethanolic solution of dry hydrogen chloride for 1 minute led to recovery of starting material, whereas heating it with polyphosphoric acid led to tar formation.

(b) The phenylhydrazone (A) (0.5 g.) and anhydrous zinc chloride (2.5 g.) were heated to 170° (oil bath) and kept at that temperature for 1 hour. The cooled mass was treated with water and then with an excess of 15% aqueous sodium hydroxide, the residue was filtered, washed repeatedly with water, and extracted with boiling 70% ethanol. The filtered extract was evaporated down till crystallization occurred, giving the crude phenylhydrazone (B) (0.31 g.), m.p. 199–200°, raised to 207–208° on recrystallization from dilute ethanol. The I.R. spectrum was identical with that of the product obtained as under (a).

#### *Alkaline Hydrolysis of Phenylhydrazone (A)*

The hydrazone (0.5 g.) was boiled under reflux for 10 hours with a solution of potassium hydroxide (1.1 g.) in 60% ethanol (12 ml.). The alcohol was partially evaporated and replaced by water, the hot solution filtered, made just acid with glacial acetic acid, and kept overnight, when the impure amino acid, contaminated with silica, had separated. Recrystallization from a small volume of 90% ethanol gave colorless crystals (0.2 g.) of 5-amino-3-methyl-2-oxopentanoic acid 2-phenylhydrazone, m.p. 172–173° (effervescence). Calc. for  $C_{12}H_{17}O_2N_3$ : C, 61.3; H, 7.2. Found: C, 61.1; H, 7.3.

#### ACKNOWLEDGMENT

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## DEOXYMERCURATION<sup>1</sup>

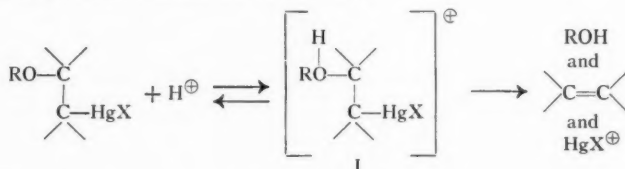
O. W. BERG, W. P. LAY, A. RODGMAN, AND G. F. WRIGHT

### ABSTRACT

The conversion of several stereoisomeric oxymercureals to alkenes (deoxymercuration) has been studied with hydrogen chloride in anhydrous and near-anhydrous methanol. In each instance the addition of water decreases the second-order rate. In benzene the addition of water to the anhydrous system first accelerates and then decreases the reaction rate. These results have been interpreted in support of molecular rather than ionic participation by hydrogen chloride. Since molecular participation requires the  $\uparrow\uparrow$  arrangement of alkoxy and chloromercuri groups for easy reaction it follows that oxymercuration also follows a molecular and not a "mercurinium ion" mechanism in the normal reaction.

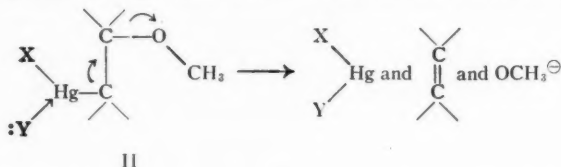
The decomposition of 2-oxyorganomercuric salts to mercuric salts and alkenes has been called deoxymercuration (11). It is a much milder reaction than is the scission of simple alkylmercuric salts, some of which resist prolonged heating with strong acids. This difference must be due to the vicinal oxygen linkage. Several opinions have been expressed about the manner in which this oxygen assists the scission of the carbon-mercury link. It will be seen that these opinions are closely related to the ideas of oxymercuration formation. For this reason a decision about the manner in which deoxymercuration occurs ought to specify the mechanism of oxymercuration.

According to Whitmore (20) deoxymercuration is induced by formation of an oxonium salt, I, which then decomposes into an alcohol, an alkene, and a mercuric monocation (where X is an acid substituent bound covalently).



According to this mechanism the rate of deoxymercuration ought to be dependent on the strength of the acid used in the reaction. This dependence on acid strength has been confirmed by experiment (11).

According to another, more recent, opinion the reaction is of the " $E_2$  elimination" type (22) in which an anion is presumed to coordinate with the mercurial (II) to force the

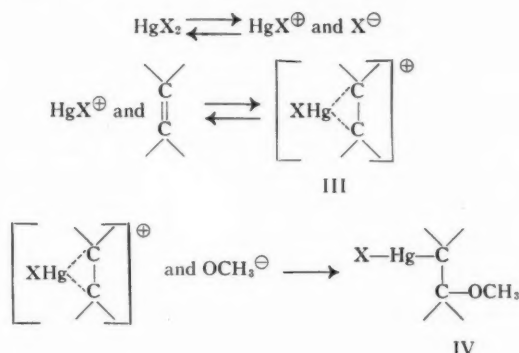


indicated electronic displacement. Presumably the experimental basis for this scheme lies in the early work of Sand and Breest (15) and a recent reconsideration of it (14). However these experiments were inconclusive. Moreover it has been shown (11) that deoxymercuration by hydrogen chloride in methanol is insensitive to addition of sodium chloride or mercuric chloride. Actually no factual proof of the  $E_2$  scheme exists.

<sup>1</sup>Manuscript received August 7, 1957.

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

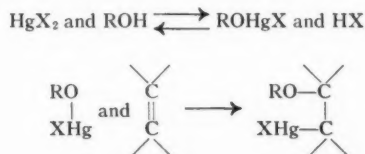
The scheme may have been revived for several reasons. First it is essentially the reversal of a popular mechanism for oxymercuration (9). These authors propose that a mercuric monocation coordinates with an alkene to give an "alkanemercurinium" ion, III, which reacts with an alkoxide ion to yield the oxymercurial, IV.



Secondly, it may be noted that the final reaction of this series involves an inversion (postulated also for the deoxymercuration) from which a *trans* ( $\uparrow\downarrow$ ) oxymercurial would be formed. The mechanism received strong support from an X-ray diffraction study (4) in which  $\alpha$ -2-methoxycyclohexylmercuric chloride was assigned the  $\uparrow\downarrow$  configuration. However, it is now realized that this X-ray diffraction study is non-definitive because the ring constellation cannot be discerned adequately in the presence of several heavy atoms. If, instead of the orthodox "crown" ring, the "flexible" cyclohexane ring (8, 7) is assumed, the location of the ring substituents may be a consequence of the ring deformation rather than of substituent configuration. Attempts to refine the structures so as to locate the ring carbon atoms more concisely than in the original study have proved to be fruitless.

However, the inversion mechanism does account satisfactorily for the experimental observation that in certain circumstances the deoxymercuration is stereospecific. When the single diastereomeric oxymercurial produced from a single geoisomer is treated with concentrated hydrochloric acid the single geoisomer is regenerated without contamination (24). Inspection of the postulated mercurinium ion shows that it will be involved stereospecifically in oxymercuration, as also will the  $E_2$  reaction specified for deoxymercuration. Moreover, the conformation required for the inversion reactions should be more favorable in one diastereomer than in another, and in many instances this difference in reactivity is observed. Thus it remains only to demonstrate that the ionic species significant to these mechanisms actually are available in the reacting systems.

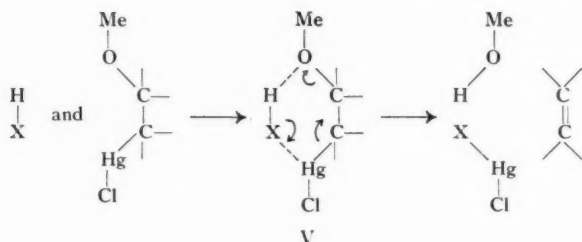
There is evidence against the direct participation of ionic species in the oxymercuration of alkenes. According to these studies (12) the reacting species is a basic mercuric salt which undergoes a four-center addition to the alkene.



It may be seen that this mechanism also satisfies the experimental requirement of a

second-order stereospecific reaction but it differs from the ionic inversion mechanism because it involves direct ( $\uparrow\uparrow$ ) addition rather than  $\uparrow\downarrow$  addition.

This mechanism, essentially molecular\* rather than ionic, has its counterpart in deoxymercuration, where a molecule of hydrochloric acid ( $X = Cl$ ) is thought to coordinate with the alkene to form a six-atom "quasi-cyclic" intermediate, V. In V the



electronic redistribution causes scission to the products. It may be seen that these explanations that are based on direct rather than inverse addition also imply stereospecificity, either of product or of reaction rate. Actually the direct ( $\uparrow\uparrow$ ) explanation fits better the oxymercuration of stilbene and isostilbene and the deoxymercuration of the corresponding two diastereomeric methoxymethylmercurials than does the inverse mechanism (23). However, one essential difference in the two mechanisms involves ion participation in one but not in the other. This criterion has been evaluated in the present report.

The deoxymercuration described above have involved hydrochloric acid. To some, this might seem to involve high ion concentration although it is evident to the experimenter, by the presence of hydrogen chloride in the gas phase above these deoxymercuration systems, that molecular hydrogen chloride must be present. Moreover, the deoxymercurating agents do not need to be strong acids. For example,  $\alpha$ -2-methoxycyclohexylmercuric chloride reacts rapidly in methanol with isopropylmercaptan. Although the  $K_A$  of this mercaptan in water is probably smaller than that of acetic acid (toward which the mercurial is reasonably stable at 25°) the precipitation of chloromercuric isopropylmercaptide is immediate. Steric convenience ought to be involved, and this effect is typified by a quasi-cyclic intermediate like IV in which HX would be isopropylmercaptan.

It is convenient to deoxymercurate in a solution consisting of methanol and concentrated hydrochloric acid but this stereospecific system may contain ionic as well as molecular species. As the water content of the system is decreased, the extent of ionization ought to become minimal. Therefore it is of interest to measure the rate of deoxymercuration in anhydrous and near-anhydrous methanol and this has been done by use of the colorimetric analysis for reacting systems of oxymercurials (3, 12).

The deoxymercuration of  $\alpha$ -2-methoxycyclohexylmercuric halides by the appropriate halogen acids are recorded in Table I. In anhydrous methanol the reaction is second-order and very rapid but the rate is decreased markedly by the addition of a few per cent of water. Comparison of the rate constants shows that the deoxymercuration is relatively insensitive to the halide involved in the reaction although the order of reactivity is roughly paralleled by the dipole moments of the three halides in dioxane solution (2). The  $\beta$ -2-methoxycyclohexylmercuric chloride, which should be sterically unfavorable toward deoxymercuration, does indeed react with hydrogen chloride in anhydrous methanol at

\*This term is applied to a substance which acts as a stereochemical unit and therefore will include the category of "ion-pair".



least 100 times slower than the  $\alpha$ -diastereomer even when the concentration is increased 15-fold. However, this slow rate is decreased at least 10-fold by addition of 1% of water.

TABLE I  
DEOXYMERCURATION OF  $\alpha$ -2-METHOXYCYCLOHEXYLMERCURIC HALIDES (RHgX,  $1.0 \times 10^{-3}$  MOLE/LITER) BY HYDROGEN HALIDES, HX, IN 96:4 METHANOL-WATER OR METHANOL AT 25°

X	HX, mole/liter $\times 10^{-3}$	Medium		K, liters/mole. sec.
		CH <sub>3</sub> OH	H <sub>2</sub> O	
Cl	1.0	100	0	3.53
Cl	1.0	96	4	0.65
Br	0.5	96	4	0.75*
Br	1.0	96	4	0.74
Br	2.0	96	4	0.76
I	0.5	96	4	0.72
I	1.0	96	4	0.70
I	2.0	96	4	0.71

\*Rate constants for bromides and iodides are calculated from early stages of the reaction; the rate decays slightly in later stages.

A similar effect is observed during the deoxymercuration of either of the diastereomeric 2-methoxy-1,2-diphenylethylmercuric chlorides. The  $\beta$ -diastereomer (derived from *trans*-stilbene) in anhydrous methanol follows rapid second-order kinetics ( $k = 2.1$  liters mole<sup>-1</sup> sec.<sup>-1</sup>) and is 80% complete within an hour. Fig. 1 shows that this rate, determined by analysis after 45 minutes of reaction time, is decreased according to the amount of water present in the methanol. The  $\alpha$ -diastereomer (derived from *cis*-stilbene) is deoxymercured more slowly, and it is necessary to use methanol solutions four times as strong as those 0.001 molar in mercurial and in hydrogen chloride which were used for the reaction with the  $\beta$ -diastereomer. Fig. 2 shows that the deoxymercuration rate of the  $\alpha$ -diastereomer also decreases with increasing amounts of water in the methanol. It may be of interest that the rate is essentially constant when more than 6% of water is present. This

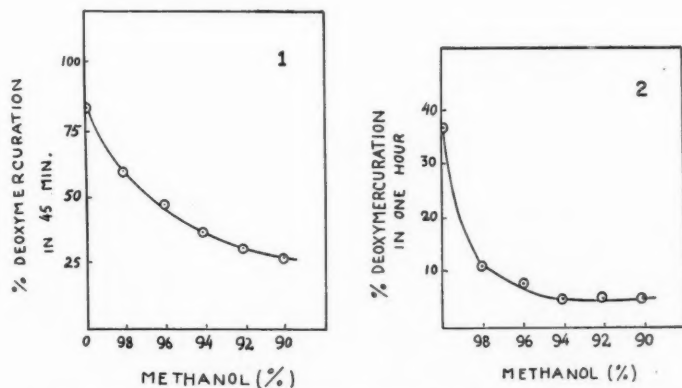
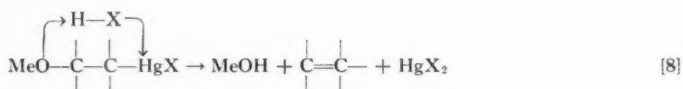
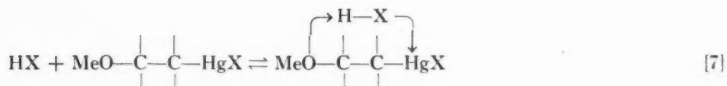
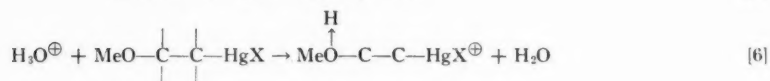
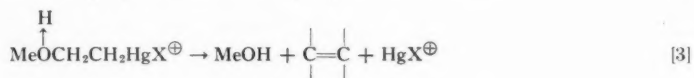
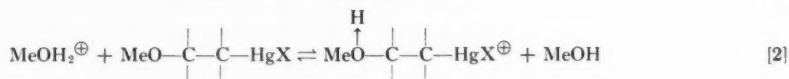


FIG. 1. Effect of water on the amount of deoxymercuration of  $\beta$ -1-chloromercuri-2-methoxy-1,2-diphenylethane during 45 minutes at 25°. [HCl] = [mercurial] = 0.001 mole/liter.

FIG. 2. Effect of water on the amount of deoxymercuration of  $\alpha$ -1-chloromercuri-2-methoxy-1,2-diphenylethane during 60 minutes at 25°. [HCl] = [mercurial] = 0.004 mole/liter.

level is about the same as that reported for the minimum in limiting equivalent conductance for hydrogen chloride in aqueous methanol (16).

The following set of equations describe the chemistry which thus far has been reported here:

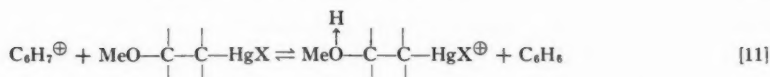


Among these, equations [1], [2], [3], [7], and [8] represent reactions in anhydrous media, while [4], [5], and [6] represent reactions in which water is present. Since the addition of water decreases the rates of deoxymercuration by hydrogen chloride that are described in the report, it is doubtful that equation [6] is significant to these reactions. On the other hand the diminution of molecular hydrogen chloride by increasing amounts of water according to equation [4] would account for the decreasing rate of deoxymercuration in this circumstance if equations [7] and [8] are valid. The expectation conforms with the observation of Shedlovsky and Kay (16) that the ionization of hydrogen chloride seems to decrease as the alcohol content of methanol-water systems increases.

The numerical data of this latter paper (16) indicate that  $10^{-3}$  molar solution should contain slightly more than 1 mole per cent of molecular or ion-pair hydrogen chloride. Reaction according to the equations [7] and [8] is thus plausible. However, the experimental results may also be explained in terms of equations [1], [2], and [3], assuming that the concentration of methoxonium ion is reduced by addition of water according to equation [5]. Actually the paucity of information respecting the true composition of the methanol-hydrogen chloride system makes a choice between the two mechanisms relatively meaningless except insofar as the results may be compared with those in a solvent of lower dielectric constant.

We have chosen to use benzene for this comparison. For our studies in this solvent we have considered the following additional equations:





It is evident from equations [1]–[11] inclusive that the use of benzene includes the complication that methanol is released as one of the products. Partly for this reason the kinetic data are not very reproducible and only the first stages of the reaction give useful data. The rate constants calculated from these data may be expected to be in error on the low rather than on the high side because of inadvertent admission of water vapor, even though atmospheric contamination was avoided vigorously.

According to electrical polarization studies (17) with hydrogen halides in benzene there seems to be no evidence for the phenyl cation. If it exists at all the concentration must be extremely low. Deoxymercuration in benzene via the phenyl cation ought therefore to be inordinately slow. Moreover, an initially slow rate ought to be enhanced if the reaction proceeds by an ionic mechanism because of methanol which appears as a product. Actually the rate constant for deoxymercuration of  $\alpha$ -2-methoxycyclohexylmercuric chloride in anhydrous benzene (described below) is greater than that in anhydrous methanol; also there is no indication of autocatalysis.

The reaction of  $\alpha$ -2-methoxycyclohexylmercuric chloride in anhydrous benzene is too fast for convenience, and solutions not stronger than  $2.0 \times 10^{-4}$  molar in mercurial and hydrogen chloride must be used in order to follow the reaction kinetically. Because of analytical difficulties prior to the actual colorimetric reading and because of hygroscopicity the numerical value of the second-order rate constant ( $5.6 \text{ liters mole}^{-1} \text{ sec}^{-1}$  at this low concentration is uncertain. However a comparison of this slope (*A*, Fig. 3) with *B* ( $2.2 \text{ liters mole}^{-1} \text{ sec}^{-1}$ ) and *C* ( $1.6 \text{ liters moles}^{-1} \text{ sec}^{-1}$ ) in which approximately  $3 \times 10^{-3} \text{ mole liter}^{-1}$  of water is included with the benzene shows that this deoxymercuration is strongly inhibited by water.

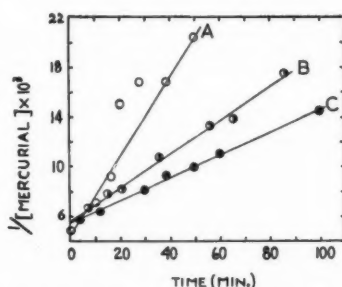


FIG. 3. Second-order rate constants ( $25^\circ$ ), deoxymercuration in benzene, anhydrous (O) or containing about  $3 \times 10^{-3} \text{ mole/liter}$  water (◐, ●).

According to this behavior deoxymercuration in benzene does not involve freely-mobile ions which can enter into second-order rate processes. On the other hand, the alternative to a free ionic agent is not simple. Perhaps it should not be expected to be simple. The enhanced electric moment of hydrogen chloride in benzene over the moment in the gaseous state indicates association of the halide with the solvent (17), and self-association together with the solvent is not rigorously excluded. Indeed Beckmann and Lockemann in their classical study (1) show that hydrogen chloride seems to associate in anhydrous benzene and that the extent of association (1.75–2.79) decreases (to 1.16) as very small amounts

of water are added progressively. Therefore evidence for equation [9] exists and seems to be involved in deoxymercuration studies with the two 2-methoxy-1,2-diphenylethylmercuric chloride diastereomers.

The  $\beta$ -diastereomer of 2-methoxy-1,2-diphenylethylmercuric chloride reacts more slowly with hydrogen chloride in benzene than does  $\alpha$ -methoxycyclohexylmercuric chloride, so solutions  $1.5\text{--}2.0 \times 10^{-3}$  molar in the stilbene mercurial and in hydrogen chloride may be used. Although this deoxymercuration is thus easier to study in respect of water content it is, unfortunately, subject to strong catalytic acceleration by mercurous chloride. Since this  $\beta$ -mercurial tends spontaneously (especially in light) to decompose into mercurous chloride, and also because of the catalytic effect of liberated methanol, the reactions may be studied only qualitatively. Fig. 4 shows that the rate is decreased by

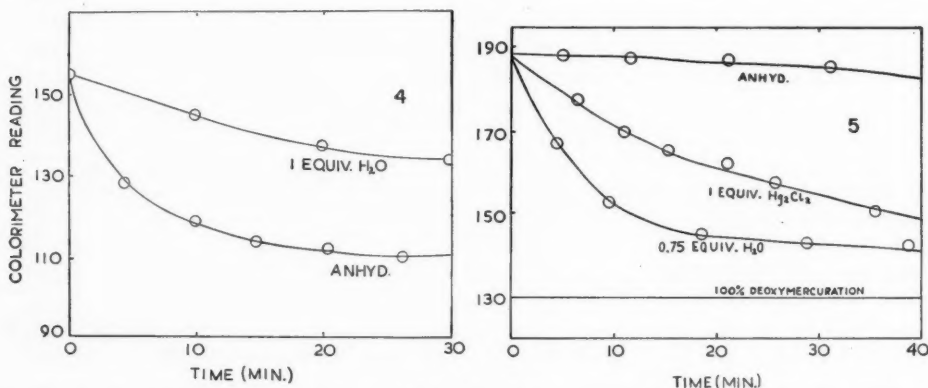


FIG. 4. Deoxymercuration of  $\beta$ -2-methoxy-1,2-diphenylethylmercuric chloride  $2 \times 10^{-3}$  molar at  $25^\circ$  by hydrogen chloride  $2 \times 10^{-3}$  molar.

FIG. 5. Deoxymercuration at  $25^\circ$  of  $\beta$ -2-methoxy-1,2-diphenylethylmercuric chloride  $2.0 \times 10^{-3}$  molar in benzene.

addition to the anhydrous system ( $2 \times 10^{-3}$  molar in mercurial and acid) of a molar excess of water. On the other hand the addition of less than a molar equivalent of water to the anhydrous system causes an increase in rate. The latter behavior is shown in Fig. 5. This diagram includes also an example of the accelerating effect of mercurous chloride, which we shall not now attempt to explain. However, with respect to water it seems reasonable to suggest that the enhancement of rate by addition of 0.75 equivalent involves the reversal according to equation [9] of the association observed by Beckmann and Lockemann, while the decreased rate with one or more equivalents of water is caused by loss of molecular hydrogen chloride because of ionization according to equation [4].

The effect of water in benzene has also been studied in the deoxymercuration of  $\alpha$ -2-methoxy-1,2-diphenylethylmercuric chloride by hydrogen chloride. In this instance the analytical method is a manometric one depending on diminution of the vapor pressure of hydrogen chloride as it is consumed in the reaction. The record (Fig. 6) of an experiment in anhydrous benzene versus a benzene solution containing less than one molar equivalent of water shows its accelerating effect to be similar to that observed for the  $\beta$ -diastereomer. Not shown is a curve demonstrating that mercurous chloride also accelerates the deoxymercuration of the  $\alpha$ -diastereomer.

In summary it would seem that if deoxymercuration is faster in benzene than in methanol, if common ion effects are not found in the latter medium, and if the retarding

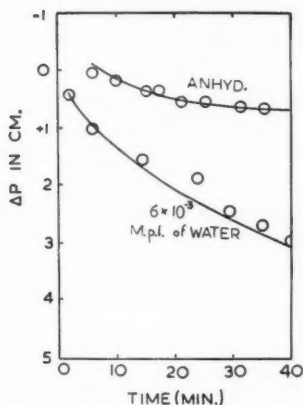


FIG. 6. Manometric analysis, deoxymercuration at 25° of  $\alpha$ -2-methoxy-1,2-diphenylethylmercuric chloride 0.01 molar by hydrogen chloride 0.01 molar.

effect of water is comparable in both media, then the improbability of an ionic mechanism in benzene renders improbable an ionic mechanism for all of these stereospecific deoxymercuration. However, it remains to prove that the reaction in benzene is as stereospecific as it is in methanol. This similarity has now been established by isolation of *cis*-stilbene uncontaminated by the *trans* isomer when  $\alpha$ -2-methoxy-1,2-diphenylethylmercuric chloride is treated with one equivalent of hydrogen chloride in benzene.

It should be noted that the non-ionic deoxymercuration is specified only for the stereospecific reactions. Actually we have succeeded in producing a few per cent of *trans*-stilbene from the  $\alpha$ -diastereomer by treatment with a 1:1 mixture of concentrated hydrochloric acid in methanol. Of course we cannot attribute the slight non-stereospecificity to an ionic deoxymercuration because *cis*-stilbene might have been the initial product which then was isomerized by the acidic medium. But also the non-stereospecificity may be due to the ionic reaction specified by Whitmore.

Such an ionic reaction may also apply to the very slow deoxymercuration of some  $\beta$ -oxymercurials in which the configuration is unfavorable to a quasi-cyclic transition state. Likewise it may apply to deoxymercuration by acids other than the hydrogen halides. But it does not apply to the deoxymercuration which has the same stereospecific behavior as does the corresponding oxymercuration. Both of these processes seem to involve molecular reactants. Therefore both should require *cis* ( $\uparrow\uparrow$ ) configuration in the mercurial. It follows that the "inversion" mechanism is not adequate to describe either oxymercuration or deoxymercuration, in respect of alkenes such as are considered in this report.

#### EXPERIMENTAL\*

##### $\alpha$ -2-Isopropoxycyclohexylmercuric Chloride

To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 30 ml. of propanol-2 was added 0.90 g. (0.011 mole) of cyclohexene. After 3 hours, filtration into 25 ml. of 5% aqueous sodium chloride at 0° C. precipitated 3.05 g. (80%) of the isopropoxymurcurial, m.p. 90.5–91.5° C. Crystallization from absolute ethanol (20 ml./g.) raised the melting point to 94.8–95.5° C. Calc. for  $C_9H_{17}ClHgO$ : C, 28.7; H, 4.52; Hg, 53.2. Found: C, 28.4; H, 4.68; Hg, 52.2.

\*Melting points have been corrected against reliable standards. X-Ray diffraction data have been obtained with  $Cu K\alpha$  (Ni filtered) radiation at  $d$  spacings in Å at visual relative intensities  $I/I_1$ .

*$\alpha$ -2-Alkoxy cyclohexylmercuric Halides Used in Kinetic Studies*

These oxymercurials, prepared by standard procedures, were purified to melt as shown in Table II.

TABLE II  
MELTING POINTS OF 2-ALKOXYCYCLOHEXYLMERCURIC HALIDES,  $\text{ROC}_6\text{H}_{10}\text{HgX}$

Diastereomer	R	X	M.p., ° C.	Reference
$\alpha$	Me	Cl	115.2-116.0	(25)
$\beta$	Me	Cl	114.1-114.5	(24)
$\alpha$	Et	Cl	60.8-61.5	(5)
$\alpha$	Pr	Cl	57.5-58.5	(12)
$\alpha$	<i>t</i> -Bu	Cl	115.0-116.0	(5)
$\alpha$	$\text{MeOC}_2\text{H}_4$	Cl	121.5-122.5	(12)
$\alpha$	H	Cl	153.0-153.6	(5)
$\alpha$	Me	Br	114.0-114.5	(13)
$\alpha$	Me	I	81.4-82.0	(6)

*Deoxymercuration Using Benzoyl Chloride**A. With  $\alpha$ -2-Methoxy-1,2-diphenylethylmercuric Chloride*

To 1.12 g. (0.0025 mole) of this mercurial in 15 ml. of ethanol-free anhydrous chloroform was added 0.29 ml. (0.0025 mole) of freshly distilled benzoyl chloride, b.p. 197° C. After 96 hours, 0.66 g. (97%) of mercuric chloride was filtered off. Vacuum evaporation of the filtrate left 0.80 g. of oil with the odor of methyl benzoate. It was refluxed with 20 ml. of 10% aqueous sodium hydroxide for 270 minutes, then steam-distilled. Etherous extraction (45 ml.) of the distillate removed 0.42 g. of *cis*-stilbene (89%), m.p. 3.5-6.0° C. This geoisomer (0.0022 mole) was characterized by treatment with 0.70 g. (0.0022 mole) of mercuric acetate in 15 ml. of anhydrous methanol for 5 hours, followed by filtration into 25 ml. of 10% aqueous sodium chloride. A mixture melting point of the precipitate (0.85 g., 70%, m.p. 142.5-143.5° C.) with  $\alpha$ -methoxydiphenylethylmercuric chloride was not lowered.

*B. With  $\beta$ -2-Methoxy-1,2-diphenylethylmercuric Chloride*

To 2.24 g. (0.005 mole) of this mercurial in 25 ml. of ethanol-free chloroform was added 0.58 ml. (0.005 ml.) of freshly-distilled benzoyl chloride, b.p. 197° C. After 1 day 1.34 g. (98%) of mercuric chloride was filtered off. Vacuum evaporation of the filtrate left a semisolid oil (1.55 g.). This was crystallized from 8 ml. of ethanol, 0.71 g. (79%) of *trans*-stilbene, m.p. 122.5-124° C., authenticated by mixture melting point.

*C. With  $\alpha$ -2-Methoxycyclohexylmercuric Chloride*

To 3.49 g. (0.01 mole) of this mercurial in 25 ml. of ethanol-free chloroform was added 1.40 g. (0.01 mole) of freshly-distilled benzoyl chloride. After 18 hours, 2.58 g. (95%) of mercuric chloride was filtered off. Vacuum evaporation of the solvent left an oil which was extracted with water. The oil, 1.35 g. (99%), was then distilled at 196-198° C. This methyl benzoate (1.10 g., 81%) was characterized by saponification; acidification precipitated 0.78 g. (87%) of benzoic acid, authenticated by mixture melting point.

The use of benzoyl chloride rather than gaseous hydrogen chloride is a convenient variation for stereospecific deoxymercuration. However, there is evidence (by Mr. Paul Chu) that the reaction is not a simple one; indeed it is catalyzed by mercuric chloride, which may be present in trace amounts in the chloromercurials. In relation to the catalytic action it is of interest that the solubility of mercuric chloride in chloroform is enhanced by the presence of an organochloromercurial which is dissolved in the chloroform.



*Deoxymercuration Using Hydrogen Chloride with  $\alpha$ -2-Methoxy-1,2-diphenylethylmercuric Chloride*

*A. In Anhydrous Benzene*

To 4.47 g. (0.01 mole) of mercurial in a 250-ml. distilling flask was added 60 ml. of a 0.195 *N* (0.012 mole) solution of hydrogen chloride in benzene during 3 minutes. Mercuric chloride was deposited during this addition; evidently reaction is rapid. After 7 minutes more the solvent was vacuum-evaporated with swirling at 25° C. In a short time the solvent was gone and the residue was quickly treated with excess of 10% aqueous alkali. The *cis*-stilbene was taken up by five washings with ether. The extract, dried by potassium carbonate, was evaporated, 1.62 g., and distilled, b.p. 140–142° C. (14 mm.),  $n_D^{20}$  1.6217, 1.51 g. (84%), leaving no *trans*-stilbene.

*B. In Aqueous Methanol*

The same amount of mercurial was stirred 12 hours at 25° C. in 90 ml. of methanol plus 90 ml. of concentrated hydrochloric acid. The system, containing oil droplets, was diluted to 700 ml. with water and thrice extracted with 90-ml. lots of ether. The extract, dried by calcium chloride, was vacuum-evaporated, and the residue chromatographed from commercial hexane on a 12 cm. by 0.8 cm. alumina column (activated at 450° C.). After 90 ml. of eluate the column was extruded, the *trans*-stilbene located by permanganate streak, and removed from the zone by ether. Evaporation left 10 mg. of *trans*-stilbene, m.m.p. 120–122° C., authenticated by mixture melting point. The column eluate yielded 1.37 g. of *cis*-stilbene, which was reconverted to the  $\alpha$ -mercurial, crude m.p. 143–144° C.

*Chloromercuric Isopropylmercaptide*

To a solution of 2.85 g. (0.008 mole) of  $\alpha$ -2-methoxycyclohexylmercuric chloride in 60 ml. of methanol was added 0.99 g. (0.013 mole) of isopropylmercaptan. A voluminous white precipitate formed immediately. It was filtered off, washed with methanol (30 ml.), and then with ether (60 ml.), 3.11 g. (100%) of infusible chloromercuric isopropylmercaptide. Calc. for  $C_3H_7ClHgS$ : C, 11.6; H, 2.25. Found: C, 12.1; H, 2.41.

Identical results were obtained with ethylmercaptan. This compound was regenerated by acidification of the infusible precipitate with hydrochloric acid.

*Kinetic Measurements*

These were carried out at  $25.0^\circ \pm 0.1^\circ \text{C}$ .

*A. Reagents*

The methanol was purified under nitrogen by Lund and Bjerrum's method (10) to be peroxide-free ( $\text{TiCl}_3$ ) and aldehyde-free (Schiff reagent). The benzene, purified by refluxing and distillation from sodium under nitrogen, was anhydrous and peroxide-free according to test with sodium benzophenone ketyl. The hydrogen chloride and hydrogen bromide were dried by passage through concentrated sulphuric acid and then through anhydrous aluminum chloride. The diphenylthiocarbazon (dithizone) was purified by the method of Winkler (21, 18).

*B. The Apparatus Used for Anhydrous Reactions*

The essential pieces of apparatus are shown as the storage burette in Fig. 7 and the reaction flask in Fig. 8. The storage burette, after thorough drying in a nitrogen stream, is filled with 160 ml. of benzene in the tubular absorber (195×20 mm. with fritted glass disperser) and the spherical chamber (68 mm. diameter) above it to a level just below the inlet from the top stopcock. Then hydrogen chloride is passed in through the horizontally-projecting conical joint by distillation (using a dry-ice bath as a source of heat) from a

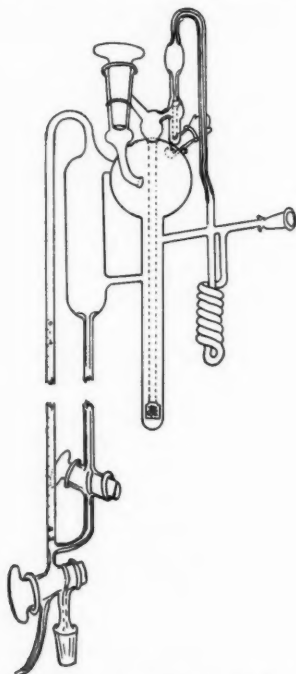


FIG. 7. The storage burette for hydrogen chloride in benzene or methanol.

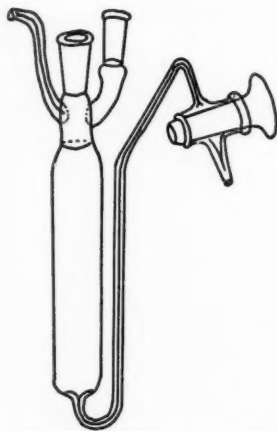


FIG. 8. The deoxymercuration vessel for kinetic studies.

trap in which the acid has been condensed by use of liquid air. When the top stopcock is closed and the three-way stopcock at the bottom of the burette is open hydrogen chloride will pass through the benzene. Finally after 30 minutes sufficient acid has been absorbed. The inlet spiral is immersed in a liquid air bath while the source of hydrogen chloride is

removed, the three-way stopcock having been closed. The latter is now reopened while a stream of dry nitrogen is passed through the horizontal inlet tube (the top stopcock being open) in order to sweep excess hydrogen chloride away from the area above the benzene solution. Then, all stopcocks being closed, the apparatus is tilted to transfer 100 ml. of the benzene solution into the storage reservoir (155×38 mm.) whence it may be standardized in the 10 ml. microburette by sample withdrawal from the plain outlet at the three-way stopcock. During all these operations the vents from the apparatus are protected from moisture by means of connections with U-tubes immersed in liquid air. All interchangeable joints are graphite-lubricated.

The reaction flask (Fig. 8) is constructed with an attachment joint to the burette, a second joint through which the solid mercurial sample is introduced by tipping from a hollow interchangeable stopper at the appropriate time, a dry-gas inlet tube and a capillary stopcock-closed outlet tube from the bottom. With these attachments the vessel does not need to be removed from the thermostat during reaction, the samples being withdrawn by rubber bulb inlet pressure which forces them out via the capillary stopcock into a cup. A definite aliquot is then withdrawn by pipette from the cup. The subsequent colorimetric procedure has been described previously (3, 12). Further detail is available in Mr. Berg's M. A. thesis.

#### C. The Manometric Apparatus

A differential manometer of the Warburg (19) type was modified by addition of an interconnecting stopcock between the reaction side and the compensator side in order to equilibrate the gas phase before the sample tube containing solid mercurial was inverted into the benzene - hydrogen chloride solution. Transferral of this solution to reaction and compensator flask from its preparative source (essentially the burette and reaction flask described above) was accomplished through serum caps via a hypodermic syringe.

#### D. Effect of Water in Methanol on Deoxymercuration

Into each of six 10 ml. volumetric flasks containing either 0, 0.2, 0.4, 0.6, 0.8, or 1.0 ml. of water was added 0.52 ml. of anhydrous methanol which was 0.0194 *N* in hydrogen chloride. Then 2 ml. of 0.005 *M* of mercurial in anhydrous methanol was added and the flask was filled quickly to volume with methanol. After brief shaking the flask was held at 20° for 5 minutes, then 1 ml. was rapidly diluted to 100 ml. with water. Ten milliliters of the diluate was thrice extracted at once by 5 ml. portions of chloroform, then 5 ml. of the aqueous layer was analyzed colorimetrically. The percentages of deoxymercuration of  $\beta$ -1-chloromercuri-2-methoxy-1,2-diphenylethane with increasing additions of water were 83.6, 59.5, 46.3, 36.7, 30.1, and 27.2. The corresponding percentages for the  $\alpha$  diastereomer were 36.7, 10.7, 7.7, 5.2, 5.2, 5.2.

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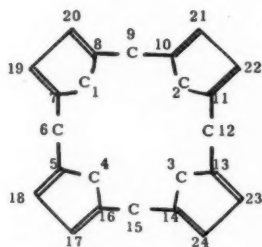
# SYNTHESIS OF PORPHYRINOGEN-LIKE COMPOUNDS (MIXED QUATERENES)<sup>1</sup>

WILLIAM H. BROWN<sup>2</sup> AND WARREN N. FRENCH<sup>3</sup>

## ABSTRACT

Three porphyrinogen-like compounds, or mixed quaterenes, have been synthesized. One quaterene contains a pyrrole and three furan residues while the others contain two pyrrole and two furan residues. The chief reaction in the preparation of these mixed quaterenes involves the condensation of a dimethylcarbinol of furan at the  $\alpha$ -position on a furan or pyrrole ring. Several previously unknown compounds of pyrrole and furan have been prepared as necessary intermediates.

The mode of condensation of furan with acetone in the presence of hydrochloric acid has recently been investigated by Ackman, Brown, and Wright (1). They found that the end product is a cyclic compound consisting of four residues each of furan and acetone after intermolecular elimination of four molecules of water. For this compound, m.p. 243°, Ackman, Brown, and Wright (1) devised the trivial name "octamethyl-tetroxa-quaterene" in which "quaterene" denotes a closed system of four cyclopentadiene nuclei linked through the 1- and 4-positions by methylene bridges.



QUATERENE NUCLEUS

Similar results have been obtained in the pyrrole series in the search for compounds having porphyrinogen-like structures. In 1886, Baeyer (2) discovered the first condensation leading to such a compound; viz., the condensation of pyrrole with acetone in the presence of hydrochloric acid. The structure of the substance, m.p. 296°, was investigated by Dennstedt and Zimmerman (3) and later by Chelintzev and Tronov (4). The compound is designated as octamethyl-porphyrinogen, or 2,2,7,7,12,12,17,17-octamethyl-21,22,23,24-tetrazaquaterene in the vernacular.

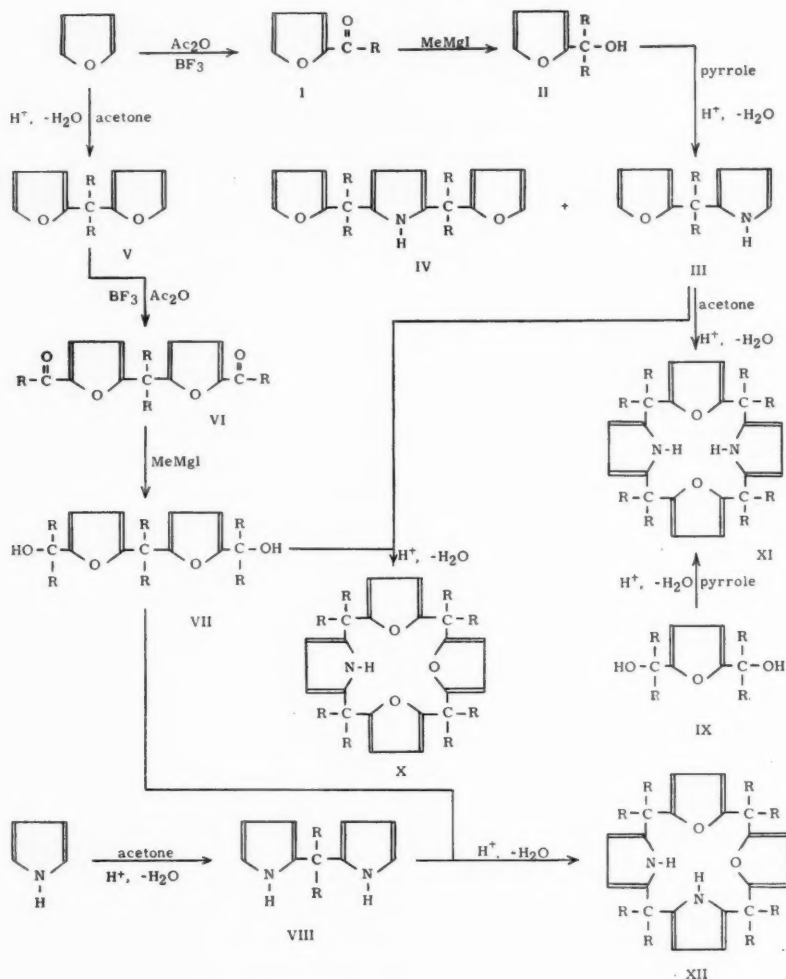
We have now succeeded in preparing mixed quaterenes containing both furan and pyrrole residues. One quaterene contains one pyrrole and three furan residues (X) while two others each contain two pyrrole and two furan residues (XI, XII). The third member of the series, containing three pyrrole and one furan residue, was not obtained

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by the methods reported in this communication. The chief reaction in the preparation of these mixed quaterenes involves the condensation of a substituted furylcarbinol at the  $\alpha$ -position on a furan or pyrrole ring.

This type of condensation has previously been demonstrated by Ackman, Brown, and Wright (1), who prepared 2,2-difurylpropane from dimethylfurylcarbinol and furan, and by Brown and Sawatzky (5), who similarly prepared difurylmethane and 1,1-difurylethane.

Since the reactions of pyrrole are, in general, similar to those of furan, it was proposed that dimethylfurylcarbinol (II) would condense with pyrrole to give an analogous product. This was indeed found to be the case. In addition to obtaining the expected



2-furyl-2-pyrrolylpropane (III), a second product, thought to be 2,5-bis(dimethylfurfuryl)-pyrrole (IV), was isolated. Increasing the ratio of pyrrole:dimethylfurylcarbinol from 1.1:1.0 to 1.5:1.0 increases the yield of 2-furyl-2-pyrrolylpropane from 20 to 40%.

Treatment of 2-furyl-2-pyrrolylpropane (III) with acetone in the presence of hydrochloric acid gives 2,2,7,7,12,12,17,17-octamethyl-21,23-diaza-22,24-dioxaquaterene (XI), m.p. 230.5°. The reaction might be expected to give rise to two products, the symmetrical quaterene (XI) and the unsymmetrical quaterene (XII), but only one was isolated. Actually, the melting point of the crude product differs only a few degrees from that of the purified product. The high purity of the crude product also suggests that III reacts as a unit and not by reversion to its constituent parts. A mixture of products, which would be expected if III decomposed, is not apparent. Furthermore, it has been shown that the product formed by the condensation of III with acetone is the symmetrical quaterene (XI), since the same compound is formed by the condensation of 2,5-diisopropyloluran (IX) with pyrrole. The unsymmetrical quaterene (XII), also containing two furan and two pyrrole residues, is formed by the condensation of 2,2-bis(5-isopropylolfuryl)propane (VII) with 2,2-dipyrrolylpropane (VIII).

Although the condensation of pyrrole with acetone has been previously investigated, the progenitor of the reaction, 2,2-dipyrrolylpropane (VIII), has not been reported. It was found that when the mole ratio of pyrrole to acetone is 2:1, a small amount of 2,2-dipyrrolylpropane is formed, along with a greater amount of tetrazaquaterene. When the reaction is allowed to proceed slowly with a pyrrole:acetone ratio of 4:1, 2,2-dipyrrolylpropane is obtained in about 21% yield.

The preparation of the other intermediate, 2,2-bis(5-isopropylolfuryl)propane (VII), utilized in the formation of 2,2,7,7,12,12,17,17-octamethyl-21,22-diaza-23,24-dioxaquaterene (XII), m.p. 260°, involved the synthesis of several previously unknown compounds. Acetylation of 2,2-difurylpropane (V) with acetic anhydride gives two products, depending on the conditions of the reaction. Under mild catalysis, such as with iodine, or when the reaction is stopped before completion under more vigorous catalysis, such as with boron trifluoride, the monoacetylated product, 2-furyl-2-(5-acetylfuryl)propane, is obtained. By allowing the reaction to proceed to completion when boron trifluoride is the catalyst, only the diacetylated product, 2,2-bis(5-acetylfuryl)propane (VI), results. The identity of each was established by preparing the semicarbazone; analysis for nitrogen indicated the presence of the mono- and di-acetylated compounds. Treatment of 2,2-bis(5-acetylfuryl)propane (VI) with methylmagnesium iodide, followed by hydrolysis, results in the expected di-tertiary alcohol (VII), which subsequently gives XII by condensation with 2,2-dipyrrolylpropane (VIII).

The third mixed quaterene, 2,2,7,7,12,12,17,17-octamethyl-21-aza-22,23,24-trioxaquaterene (X), m.p. 223°, is obtained in about 13% yield from the condensation of 2,2-bis(5-isopropylolfuryl)furan (VII) with 2-furyl-2-pyrrolylpropane (III). The preparation of X was also attempted by treating 2,5-bis(dimethylfurfuryl)pyrrole (IV) with 2,5-diisopropyloluran (IX) in the presence of hydrochloric acid. However, only resinous products resulted. Similarly, Ackman, Brown, and Wright (1) obtained only resinous products by treating 2,5-bis(dimethylfurfuryl)furan with 2,5-diisopropyloluran.

During the course of the investigation, several characteristics of the condensations leading to mixed quaterenes were observed. In general, it was found that the dimethylcarbinol of furan condenses with a furan nucleus to give a product in low yield (14%). However, the dimethylcarbinol of furan reacts quite readily with a pyrrole nucleus to form a product in good yield (69%). This points up the greater reactivity of pyrrole

$\alpha$ -hydrogen over furan  $\alpha$ -hydrogen. It was also found that dimethylfurylcarbinol does not condense with thiophene under the conditions employed. A variety of products are formed, none of which contains a thiophene residue. Apparently, the furylcarbinol condenses with itself to form several indefinite products rather than condensing with thiophene. In view of these observations, it would appear possible to prepare other mixed quaterenes by the condensation of a substituted carbinol of thiophene with a furan or pyrrole nucleus.

#### EXPERIMENTAL

All melting points have been corrected against reliable standards. Molecular weights were determined by the Rast method.

##### *Acetylfuran (I)*

The compound was prepared by the method of Heid and Levine (6) involving the acetylation of furan with acetic anhydride using a boron trifluoride catalyst (B & A Code 1471).

##### *Dimethylfurylcarbinol (II)*

The method used for the preparation of the compound was that of Reichstein, Zschokke, Gehring, and Rona (7) involving the treatment of acetylfuran with methyl Grignard reagent.

##### *2-Furyl-2-pyrrolpropane (III)*

A solution of 30 g. (0.45 mole) of pyrrole in 30 ml. of commercial absolute ethanol was placed in a 125 ml. Grignard-type flask equipped with stirrer and dropping funnel and cooled to 0° in an ice-bath. Ten milliliters of 37% hydrochloric acid solution was added slowly while the solution was being stirred. To the resulting colorless solution, 48.7 g. (0.39 mole) of dimethylfurylcarbinol was added dropwise over a period of 15 minutes. The mixture turned yellow at first, then a dark green. The ice-bath was removed and the mixture stirred for 2 hours at room temperature. The addition of 100 ml. of water resulted in the formation of two liquid phases. The lower amber organic phase was separated from the upper aqueous phase, washed until neutral with 10% sodium carbonate solution, then dried over anhydrous magnesium sulphate. The excess pyrrole was removed under diminished pressure and the residual oil fractionally distilled.

The first fraction, a colorless fluorescent oil, distilled at 96–98° (2–3 mm.) and weighed 13.6 g. (20%);  $\eta_D^{20}$  1.5330,  $d_4^{20}$  1.056. Anal. Calc. for  $C_{11}H_{13}NO$ : N, 8.00; Mol. wt., 175. Found: N, 8.00; Mol. wt., 182.

##### *2,5-Bis(dimethylfurfuryl)pyrrole (IV)*

A second fraction from the preceding distillation, a light yellow oil, boiled at 154–156° (3 mm.) and weighed 17.1 g. (31%);  $\eta_D^{20}$  1.5286,  $d_4^{20}$  1.052. Anal. Calc. for  $C_{18}H_{21}NO_2$ : N, 4.94; Mol. wt., 283. Found: N, 5.00; Mol. wt., 290.

##### *2,2-Bis(5-acetylfuryl)propane (VI)*

A solution of 20 g. (0.114 mole) of 2,2-difurylpropane (V) and 24.5 g. (0.228 mole) of 95% acetic anhydride in a 125 ml. Grignard-type flask equipped with stirrer and thermometer was cooled to 0° in an ice-bath. While the solution was being stirred vigorously, 2 ml. of boron trifluoride etherate (B & A Code 1471) was added all at once. The color of the solution changed to cherry red, then to dark purple, and the temperature slowly rose to 30° and then fell. When the ice-bath was removed, the temperature slowly rose to 70°. Stirring was continued until the reaction mixture cooled to room temperature,

then 50 ml. of water was added and stirring continued for 30 minutes. The upper aqueous phase was separated from the lower organic phase and the former extracted with three 15-ml. portions of chloroform. The chloroform extracts and the lower organic phase were combined and washed with 50 ml. of 10% sodium carbonate, 50 ml. of water, and dried over anhydrous magnesium sulphate. The chloroform was flashed off and the residue distilled under diminished pressure. The product, a viscous light yellow oil, weighed 15 g. (51%) and distilled at 178–182° (2–3 mm.). On cooling in the refrigerator, the material formed a thick gel but did not crystallize.

The disemicarbazone derivative of this compound, m.p. 235° (with decomposition), was prepared in the usual manner. Anal. Calc. for  $C_{17}H_{22}N_6O_4$ : N, 22.4. Found: N, 22.4.

#### *2-Furyl-2-(5-acetylfuryl)propane*

A solution of 20 g. (0.114 mole) of 2,2-difurylpropane and 28.2 g. (0.262 mole) of 95% acetic anhydride was cooled to 0° by means of an ice-bath and treated with 2 ml. of boron trifluoride etherate (B & A Code 1471). The temperature of the reaction mixture rose to 34°, then fell. Stirring was continued for 30 minutes with the ice-bath still in place. After being worked up as described before, the product was fractionally distilled. The first fraction, a colorless oil which crystallized in the receiver, distilled at 123–126° (2 mm.) and weighed 5.5 g. (25%). Crystallization from an ethanol–water solution gave shiny flat plates, m.p. 84.0–84.5°. Calc. for  $C_{13}H_{14}O_5$ : Mol. wt., 218. Found: 210.

The semicarbazone, which was prepared in the usual manner, had a melting point of 186.5°. Anal. Calc. for  $C_{14}H_{17}N_3O_3$ : N, 15.3. Found: N, 15.6.

#### *2,2-Bis(5-isopropylfuryl)propane (VII)*

An ethereal solution of 0.123 mole of methylmagnesium iodide was prepared. The solution of the Grignard reagent was cooled in an ice-bath and while it was being stirred vigorously, 15 g. (0.0577 mole) of 2,2-bis(5-acetylfuryl)propane was added dropwise to it over a period of 30 minutes. Stirring was continued for 2 hours at room temperature. The mixture was then poured over 150 g. of chipped ice to decompose the yellow complex. The aqueous layer was saturated with sodium carbonate and the ether decanted. After extraction with ether, the combined ether extracts were dried over anhydrous potassium carbonate. Most of the ether was removed by distillation, the remainder by passing a current of air over the cold solution. The residue was a sticky yellow solid, which was dissolved in hot hexane; the resulting solution was cooled and partially evaporated by means of a current of air. A white crystalline solid formed on the walls of the flask. After the process had been repeated three times, a total of 6.0 g. (36%) of white crystals was obtained, m.p. 91–92°.

This product was not amenable to purification for analysis by ordinary crystallization procedures since it readily decomposes with formation of an oil. The compound is assumed to be the di-tertiary alcohol based on its mode of formation and subsequent reactions. A molecular weight determination on the crude product gave a value of 308, which is in agreement with the theoretical value of 298 based on the molecular formula  $C_{17}H_{24}O_4$ .

#### *2,2-Dipyrrolylpropane (VIII)*

A solution of 67 g. (1 mole) of pyrrole and 20 ml. of commercial absolute ethanol in a 125 ml. Grignard-type flask equipped with stirrer, dropping funnel, and thermometer was cooled to 0° in an ice-bath. While the solution was being stirred, 3 ml. of 37% hydrochloric acid solution was slowly added, followed by 14.5 g. (0.25 mole) of acetone, which was added dropwise over a period of 25 minutes. The temperature was kept at 10° throughout the addition. Stirring was continued for 2 hours during which time the

solution turned yellowish-green in color. The solution was poured into 100 ml. of water and the resulting mixture neutralized with solid sodium carbonate. The upper organic phase was removed, washed with water, and dried over anhydrous magnesium sulphate. The excess pyrrole was removed under diminished pressure and the residual oil fractionally distilled from a Claisen flask to give 13.5 g. (31%) of a light yellow oil (b.p. 146–153°, 8 mm.), which partially solidified on cooling. Fractional distillation through a column as described by Bower and Cook (8) gave 9.2 g. (21%) of a colorless fluorescent oil (b.p. 125–126°, 3 mm.), which solidified in the receiver, m.p. 59°. Crystallization from petroleum ether gave rhomboid crystals but did not change the melting point. Anal. Calc. for  $C_{11}H_{14}N_2$ : N, 16.1; Mol. wt., 174. Found: N, 16.3; Mol. wt., 184.

*2,2,7,7,12,12,17,17-Octamethyl-21-aza-22,23,24-trioxaquaterene (X)*

A solution of 0.50 g. (0.00172 mole) of 2,2-bis(5-isopropylfuryl) propane (VII) and 0.30 g. (0.00172 mole) of 2-furyl-2-pyrrolpropane (III) in 5 ml. of absolute ethanol was cooled in an ice-bath. While the solution was being agitated, 0.4 ml. of 37% hydrochloric acid solution was added dropwise. A greenish-yellow color developed immediately, which soon changed to orange and then to dark brown. Solid material started to form in 15 minutes. After the solution was left for 15 hours, a sticky solid was removed by filtration. Crystallization from absolute ethanol gave 0.10 g. (13.5%) of light yellow needles, m.p. 217–220°. A second crystallization gave fine white needles, m.p. 223°. Yields are lower when the above reaction is carried out on a larger scale. Anal. Calc. for  $C_{28}H_{34}NO_3$ : N, 3.26; Mol. wt., 431. Found: N, 3.24; Mol. wt., 450.

*2,2,7,7,12,12,17,17-Octamethyl-21,22-diaza-23,24-dioxaquaterene (XII)*

A solution of 0.522 g. (0.003 mole) of 2,2-dipyrrolpropane (VIII) and 0.875 g. (0.003 mole) of 2,2-bis(5-isopropylfuryl)propane (VII) in 10 ml. of absolute ethanol was cooled in an ice-bath. To this solution was added 0.15 ml. of 37% hydrochloric acid solution. A solid began to form immediately. After 3 hours, the solid was removed by filtration and washed with ethanol to give 0.89 g. (69%) of light gray needles, m.p. 255–257° (with darkening). Crystallization from benzene (15 ml./g.) gave 0.51 g. of white needles, m.p. 260° (with darkening). Anal. Calc. for  $C_{28}H_{34}N_2O_2$ : N, 6.50; Mol. wt., 431. Found: N, 6.58; Mol. wt., 440.

*2,2,7,7,12,12,17,17-Octamethyl-21,23-diaza-22,24-dioxaquaterene (XI)*

*(a) From 2-Furyl-2-pyrrolpropane and Acetone*

A solution of 2.0 g. (0.011 mole) of 2-furyl-2-pyrrolpropane (III) and 3.0 g. (0.052 mole) of acetone in 10 ml. of absolute ethanol was cooled in an ice-bath. While the solution was being swirled, 37% hydrochloric acid solution was added dropwise. The solution became orange in color, then a deep cherry red. After 2 ml. of acid had been added, an oil began to separate. The mixture was heated to 50° during which time the oil dissolved and crystals started to form. After it was left for 30 minutes, the mixture was filtered. The residue was washed with 95% ethanol until the color had been removed (about 5 ml.) leaving 0.36 g. (15%) of fine white needles, m.p. 227.5–228.5°. Crystallization from an acetone–water solution, including treatment with charcoal, gave shiny white needles, m.p. 230.5°. Anal. Calc. for  $C_{28}H_{34}N_2O_2$ : C, 78.1; H, 7.96; N, 6.51; Mol. wt., 431. Found: C, 78.0; H, 7.83; N, 6.73; Mol. wt., 424.

*(b) From 2,5-Diisopropylfuran and Pyrrole*

The method of Ackman, Brown, and Wright (1) was used for the preparation of 2,5-diisopropylfuran (IX) from diethyl 2,5-furandicarboxylate which had been previously prepared by the dehydration of mucic acid and esterification of the product. A

solution of 0.55 g. (0.003 mole) of 2,5-diisopropylfuran and 0.20 g. (0.003 mole) of pyrrole in 10 ml. of absolute ethanol was cooled in an ice-bath. Then, while it was being agitated, 0.3 ml. of 37% hydrochloric acid solution was added. A white crystalline solid began to form immediately. The solution was colorless at first, then became a deep red. After 4 hours, the mixture was filtered and the residue washed with 5 ml. of 95% ethanol to give 0.090 g. (14%) of white needles, m.p. 228–229°. Crystallization from absolute ethanol (100 ml./g.) gave shiny white needles, m.p. 230.5°. A mixture melting point of this compound with that obtained in (a) showed no depression.

#### ACKNOWLEDGMENTS

We are grateful for financial assistance from the National Research Council of Canada for one of us (W.N.F.). The Du Pont Company of Canada has been most helpful by supplying generous quantities of furan and pyrrole.

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# SYNTHESIS OF GUANIDINE FROM UREA, AMMONIUM BENZENESULPHONATE, AND AMMONIUM SULPHAMATE<sup>1</sup>

JEAN L. BOIVIN AND MEUDE TREMBLAY

## ABSTRACT

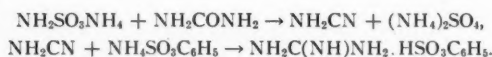
Guanidine benzenesulphonate has been obtained in yields exceeding 70% by heating urea, ammonium sulphamate, and ammonium benzenesulphonate in respective molar ratios of 1:1:0.75. The effects of temperature, proportion of reactants, and reaction time were studied batchwise. Then the process was operated on a continuous basis in a four-flask cascade reactor at temperatures between 240° and 260° C.

## INTRODUCTION

The fusion of urea with ammonium sulphamate gives rise to guanidine sulphamate in relatively low yield, and even a large excess of ammonium sulphamate does not effect the transformation in yields higher than 80% (3). Moreover, the fusion is hampered by the formation of ammonium sulphate coming out of the melt at high temperature. The presence of this insoluble salt in the fusion mixture makes a continuous process impossible.

A search has been made for a guanidine salt which would be stable up to 300° C. in the fused state and could be readily transformed into either guanidine nitrate or nitroguanidine. Sulphonic acids appeared to be suitable since they are stable and, unlike sulphamic acid, are not readily hydrolyzed. Guanidine benzenesulphonate melts at 212° C. and can be fused at 300° C. without decomposition or appearance of melamine (2). Moreover, guanidine benzenesulphonate is less soluble in water than guanidine nitrate and can be crystallized from it.

Guanidine benzenesulphonate can be obtained by the reaction between urea, ammonium sulphamate, and ammonium benzenesulphonate. The fusion of urea and ammonium sulphamate gives cyanamide and ammonium sulphate (1); cyanamide then reacts with ammonium benzenesulphonate to yield guanidine benzenesulphonate according to the following equations:



A study of the effect of temperature, molar ratio of reactants, and reaction time was made batchwise by heating the mixture in a flask, and on a continuous basis in a four-flask cascade reactor. It was observed that the addition of ammonium sulphate to the urea - ammonium benzenesulphonate - ammonium sulphamate mixture did not appreciably change the fluidity of the melt at the synthesis temperature, because of its relative solubility in the fused mixture. The crude guanidine benzenesulphonate thus formed was isolated by crystallization from water and melted at 212° C. A mixed melting point determination with an authentic sample was not depressed.

## EXPERIMENTAL AND RESULTS

### *Preparation of Guanidine Benzenesulphonate*

#### *Batch Process*

The preliminary experiments were directed to the study of the effect of temperature, molar ratio of reactants, and time of the reaction on the yield. The reaction was carried

<sup>1</sup>Manuscript received October 23, 1957.

Contribution from Canadian Armament Research and Development Establishment, Valcartier, Quebec.



out in a three-necked flask equipped with a stirrer, a thermometer, and gas inlet. Heating was accomplished by means of a heating mantle. The mixture of ammonium sulphamate, ammonium benzenesulphonate, and urea melted at about 100° C., and at 180–200° C. an exothermic reaction took place with evolution of gases and the formation of a sublimate. The melt was heated to the desired temperature for a period of 15 to 90 minutes. The liquid was then poured into a beaker, allowed to cool, dissolved in water, and diluted to 500 cc. in a volumetric flask. The solution was analyzed for guanidine with a solution saturated with ammonium picrate and guanidine picrate.

*Effect of reaction temperature.*—Table I shows the results obtained at different temperatures. The maximum yield of guanidine benzenesulphonate was obtained at 240° C. after a 1-hour period of heating.

TABLE I

## EFFECT OF TEMPERATURE

Urea: 15 g. (0.25 mole); ammonium sulphamate: 28.5 g. (0.25 mole); ammonium benzenesulphonate: 57.4 g. (0.25 mole)

Temp., ° C.	Time, min.	Yield from urea, %	Temp., ° C.	Time, min.	Yield from urea, %
290	30	27.0	300	60	16.0
280	"	29.6	290	"	16.5
270	"	36.3	280	"	26.3
260	"	46.3	270	"	29.7
250	"	54.9	260	"	44.0
240	"	56.2	250	"	53.3
220	"	43.0	240	"	60.0
			230	"	55.4
			220	"	53.5

*Effect of molar ratio of reactants.*—Results are summarized in Table II. Yields increased with excess of urea, but much decomposition occurred giving rise to a material insoluble in water. Yields increased also with the amount of ammonium sulphamate and remained practically constant as the proportion of benzenesulphonate was increased.

TABLE II

## EFFECT OF MOLAR RATIO OF REACTANTS

Temperature: 240° C.; time: 1 hour

Urea		Ammonium sulphamate		Ammonium benzenesulphonate		Yield from urea, %
g.	mole	g.	mole	g.	mole	
30	0.5	28.5	0.25	57.4	0.25	79.6
24	0.4	"	"	"	"	67.9
18	0.3	"	"	"	"	62.6
15	0.25	"	"	"	"	60.0
15	0.25	34.2	0.3	57.4	0.25	57.0
"	"	42.7	0.375	"	"	61.7
"	"	57.0	0.5	"	"	67.0
15	0.25	28.5	0.25	45.8	0.2	63.4
"	"	"	"	68.7	0.3	63.1
"	"	"	"	92.2	0.4	62.3

*Effect of reaction time.*—The results are shown in Table III. At low temperature (240° C.) yields were practically the same, but a 30-minute period of heating was sufficient. With longer heating times some solid separated from the melt and impaired the stirring. Higher temperatures (260° C.) required shorter times.

TABLE III

EFFECT OF REACTION TIME AT 240°, 250°, AND 260° C.  
Ammonium benzenesulphonate: 57.4 g. (0.25 mole);  
urea: 18 g. (0.3 mole); ammonium sulphamate:  
57 g. (0.5 mole)

Temp., ° C.	Time, hr.	Yield from ammonium benzenesulphonate, %
240	0.5	68.2
"	1.0	66.2
"	1.5	70.3
250	0.5	66.5
"	1.0	58.9
"	1.5	60.0
260	0.5	60.4
"	1.0	53.5
"	1.5	47.5

#### *Continuous Process*

The main object of this work was to produce guanidine benzenesulphonate on a continuous basis. A cascade reactor consisting of four 500-ml. flasks was built in such a way that molten material overflows from flask 1 to flask 4 by gravity. A stream of anhydrous ammonia was introduced at the bottom of each flask to stir the molten solid while the flasks were heated by mantles.

Runs were made by adding urea, ammonium sulphamate, and ammonium benzenesulphonate in respective molar ratios of 1:1:0.9. These molar ratios were considered to be the optimum proportions to give maximum melt fluidity. The reduced molar ratio of ammonium benzenesulphonate was sufficient to form the salt of the guanidine produced in the reaction. The residence time in the reaction flasks varied from 15 to 120 minutes at the rates of feed of 20 to 5 grams per minute respectively. The mixture was first added manually at a constant rate of 5 to 15 grams per minute. Attempts were made to introduce the same mixture by means of a screw feeder to obtain a constant rate of addition but this mixture absorbed water rapidly and became tacky, causing plugging of the screw feeder. It was found that the mixture became hygroscopic owing to the presence of urea. Two screw feeders were then used to introduce respectively urea and the mixture of ammonium sulphamate and ammonium benzenesulphonate. With this arrangement two 8-hour runs were made successfully using 10 pounds of mixture each.

The mixture was melted at 160–170° C. in the first flask and allowed to overflow to the second flask where the temperature reached 250–260° C. The reaction in the second flask was exothermic with evolution of ammonia. The liquid flowed through two more flasks to complete the reaction and was finally collected in a beaker where it solidified. After solidification, a weighed sample was dissolved in the minimum of water and analyzed for guanidine. The guanidine benzenesulphonate was also crystallized, weighed, and its purity determined. Yields of about 60 to 80% were obtained depending on the rate of feed. The results given in Table IV show that the yields obtained by adding the mixture at a constant rate from 10 to 15 grams per minute were 66 to 71% by crystallization, the product obtained being about 97% pure.

TABLE IV  
CONTINUOUS FUSIONS

Temperature of flask 1: 160–170° C.  
 Temperature of flasks 2, 3, and 4: 250° C.  
 Molar ratio of urea, ammonium sulphamate, and ammonium benzenesulphonate: 1: 1: 0.9

Estimated residence time of reaction, min.	Rate of feed, g./min.	Yield of guanidine from urea, %	
		By analysis	By cryst.
120	5	60.6–63.0	
90	7.5	68–73.9	
60	10	74.5	
60	10	75.2–81.1	66.6†
60	10*	77.5	71.0
30	15*	72.4–81.5	67.4
15	20	53.4–90.0	

\* Using two screw feeders.

† A mixed melting point with an authentic sample of guanidine benzenesulphonate (m.p. 212° C.) was not depressed.

## RECOVERY OF UNREACTED AMMONIUM SULPHAMATE

To make the synthesis more attractive, the unreacted ammonium sulphamate should be recovered. The melt obtained from the continuous reactor was dissolved in water and fractionally crystallized. Results given in Table V show that guanidine benzenesulphonate crystallized first, then on further concentration ammonium sulphate was obtained, and finally ammonium sulphamate. The separation is not very clear-cut and a more practical procedure is required to reclaim the ammonium sulphamate on a production scale.

TABLE V  
FRACTIONAL CRYSTALLIZATION OF FUSION PRODUCT  
Weight of melt used: 540 g.

Crop of crystals	Volume of solution, ml.	Weight of solid, g.	Composition of solid		
			Ammonium sulphate, %	Ammonium sulphamate, %	Guanidine ben- zenesulphonate, %
1	800	250	1.0	1.1	97.0
2	600	51.2	71.1	2.7	23.7
3	400	70.1	98.1	5.79	0.0
4	200	66.8	61.1	7.8	0.0
5	100	76.3	54.4	20.6	0.0

## DISCUSSION

The results obtained by the fusion of urea, ammonium sulphamate, and ammonium benzenesulphonate are promising. The fusion stage is sufficiently exothermic to preclude any use of external heating and the conversion of urea into guanidine is high using a stoichiometric ratio of reactants. It has been shown that the proportion of ammonium benzenesulphonate could be reduced below the stoichiometric amount with equally good results.

The use of ammonium benzenesulphonate stabilizes the guanidine formed and prevents its transformation into melamine; this stabilizing effect could otherwise be

accomplished by the use of a large excess of ammonium sulphamate. The presence of ammonium benzenesulphonate in the fusion mixture also increases the fluidity of the melt and prevents the separation of ammonium sulphate.

The presence of guanidine as its benzenesulphonate salt makes possible a continuous process which has been demonstrated in a laboratory system. Guanidine benzenesulphonate was separated easily from the salts present in the fusion mixture. However, the high stability of this salt made difficult its transformation into guanidine nitrate directly by means of ammonium nitrate or nitric acid.

This fusion has the advantage of being made at atmospheric pressure. A reactor will be easily constructed from conventional materials. No difficult heat transfer problem will arise since the reaction is self-sustaining.

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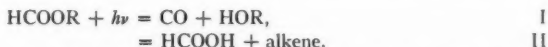
# THE PHOTOLYSIS OF ALKYL ESTERS<sup>1,2</sup>

P. AUSLOOS<sup>3</sup>

## ABSTRACT

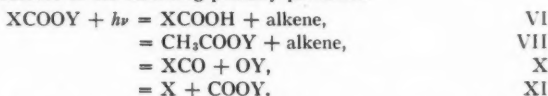
An attempt has been made to determine the primary processes in the gas and liquid phase photolysis of simple alkyl esters.

The liquid phase photolysis of methyl, ethyl, *n*-propyl, and *n*-butyl formate has been briefly investigated. Besides the dissociation processes, two intramolecular rearrangements were found to occur:



Process I takes place with approximately the same yield for all the formates studied. Process II occurs only when there is a  $\beta$ -hydrogen in the alkyl group.

An investigation of the gas and liquid phase photochemical decomposition of esters other than formates showed the existence of the following primary processes:



Processes VI and VII require  $\beta$ - and  $\gamma$ -hydrogens, respectively, in the Y and X alkyl groups.

It was found that processes I and X occur mostly at short wavelength, while the other processes take place at long wavelengths as well.

## EXPERIMENTAL

The liquids were irradiated in a quartz cell of 5 cm. diameter and 0.1 cm. depth. The cell was closed with a break seal which made it possible to attach the cell to the analysis system after each run.

Spectra taken with a Cary spectrophotometer indicated that for a 0.1 cm. path length 100% of the useful radiation was absorbed. Absorption occurred only below 2400 Å. Experiments with a Corning filter 9863, cutting off radiation below 2250 Å, reduced the rates of formation of the products by a factor of approximately 20. Absorption spectra of formates diluted with ethanol showed a maximum around 2150 Å, while the extinction coefficients were appreciably higher than those of ketones and aldehydes.

Irradiation was carried out in a quartz Dewar filled with distilled water. For a few low temperature runs, however, 3-methyl pentane was used.

The gas phase experiments were performed with a cylindrical quartz cell (5 cm. diameter, 10 cm. long) which was completely filled with a nearly parallel light beam. The low temperature runs were performed in a brass cylinder thermostat with double quartz windows. Ethyl alcohol was used as a cooling medium.

Two Hanovia (16A-13) SH-type medium pressure lamps were used in the course of this work. Because a slight change in wavelength distribution changes the relative rates of formation of the products, the number of each run is preceded by a letter *a* or *b* depending on which lamp was used. Except when stated otherwise, the incident intensity was kept constant for all the runs with lamp *a*. This allows comparison of the rates of

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<sup>2</sup>Contribution from Département de Chimie, Université Laval, Quebec, Que., and Department of Chemistry, The University of Rochester, Rochester, N. Y.

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formation of the products from one table to another. All rates are given in cc./min.  $10^{-4}$ . No absolute quantum yields were determined.

The analysis procedure was the same as described earlier (2).

The esters were obtained from Eastman Kodak Co. (White Label). Ethyl formate, methyl acetate, and methyl propionate were fractionated in a 10 plate column before distillation in the vacuum line. The other compounds were distilled and degassed in vacuum.

#### PART I. THE PHOTOCHEMICAL DECOMPOSITION OF FORMATES

##### Results

The results of runs performed in the liquid phase at constant incident intensity and varying temperatures are given in Table I.

TABLE I  
LIQUID PHOTOLYSIS OF FORMATES  
Variation of rate with temperature

	Run	Temp., ° C.	$R_{CO}$	$R_{H_2}$	$R_{CH_4}$	$R_{CO_2}$	
Methyl formate	a1	5	82.5	8.0	27.5	29.0	
	a2	31	82.0	8.0	186	160	
	Run	Temp., ° C.	$R_{CO}$	$R_{H_2}$	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{CO_2}$
Ethyl formate	a3	5	82.0	9.5	171	25.8	27.5
	a4	35	80.0	9.0	184	120	112
	a5	51	82.5	10.0	205	214	218
	Run	Temp., ° C.	$R_{CO}$	$R_{H_2}$	$R_{C_3H_6}$	$R_{C_3H_8}$	$R_{CO_2}$
<i>n</i> -Propyl formate	a6	6	74.0	7.0	305	7.0	10
	a7	32	77.0	7.0	302	36.0	41.5
	a8	50	77.0	7.0	295	70.5	84.5
	a9	74	83.0	8.0	297	180	206
	Run	Temp., ° C.	$R_{CO}$	$R_{H_2}$	$R_{C_4H_8}$	$R_{C_4H_{10}}$	$R_{CO_2}$
<i>n</i> -Butyl formate	a10	6	67.5	7.8	154	4.3	11.4
	a11	45	70.0	9.0	166	43.0	60.0
	a12	85	98.0	12.0	169	108	116

It can be seen that the rates of formation of hydrogen and of carbon monoxide change very little with temperature for each compound taken separately and show only slight variations from one compound to another.

Formates with a  $\beta$ -hydrogen in the alkyl groups have under these experimental conditions an alkene as most important product. The rates of formation of these alkenes vary only slightly with temperature, but, unlike the rates of formation of carbon monoxide, change considerably from one compound to another.

The only other products analyzed for were carbon dioxide and the hydrocarbons: methane, ethane, propane, butane, formed respectively in the photolysis of methyl, ethyl, propyl, butyl formate.

The results indicate that the rate of formation of carbon dioxide is roughly equal to that of the corresponding hydrocarbon. They both increase appreciably with increase in temperature.



The rates of formation of the recombination products ethane and butane, formed in the photolysis of methyl and ethyl formate, respectively, are not given in Table I because these products were always present in amounts too small to be measured accurately. The amount of ethane formed in experiments 1 and 2 was less than 1% of the carbon dioxide fraction. No attempt was made to determine the rates of formation of hexane and octane in the photolysis of propyl and butyl formate.

The results of a few more liquid phase experiments on ethyl formate are included in Table II. Runs 13, 14, and 15 were performed in order to obtain a rough idea of the effect on the products of a variation in the wavelength distribution. The temperature was

TABLE II  
PHOTOLYSIS OF ETHYL FORMATE

A. Liquid phase

Run	Temp., °C.	Time, min.	$R_{CO}$	$R_{H_2}$	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{CO_2}$	$\frac{R_{C_2H_4}}{R_{CO}}$	$I_{rel}$
Variation of wavelength									
b13	13	25	42.5	6.8	152	26.0	30.5	3.57	
b14*	13	70	13.0	1.4	112	32.5	35.0	7.80	
b15†	13	101	1.1	0.18	25.3	18.8	19.0	23.0	
b16*	-60	35	14.3	1.3	60.5	2.0	1.10	4.24	
b17*	-80	70	14.6	1.28	57.0	2.0	1.3	3.90	
Variation of intensity									
b18	28	13	26.7	4.63	101	62.0	58.5	3.80	1500
b19	28	88	3.15	0.68	11.9	16.4	15.9	3.80	180
b20	28	705	0.405	0.08	1.32	4.68	4.5	3.25	19
b21	28	4700	0.023	0.0036	0.067	0.505	0.512	2.85	1

B. Gas phase

Run	Temp., °C.	Time, min.	Pres- sure, cm.	$R_{CO}$	$R_{H_2}$	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_3H_8}$	$R_{C_4H_{10}}$
b22	0	45	4.1	62.0	7.7	16.6	11.8	22.0	2.45	2.0	4.3
b23	29	35	4.5	80.0	8.8	16.4	15.8	31.0	5.75	3.15	4.0
b78§	27	20	4.5	59.0	1.35	16.0	0.5	10.6	—	—	—

\*3-Methyl pentane bath.

†Corning filter 9863.

§Iodine added 0.035 cm.

kept constant. Run 14 was done with a 3-methyl pentane bath which absorbed most of the radiation below 2150 Å. In order to cut off radiation below 2250 Å, a Corning filter 9863 was used in run 15. It follows from these experiments that a change in the wavelength distribution appreciably affects the ratio  $C_2H_4/CO$ . The rates of formation of carbon monoxide and hydrogen decrease appreciably as compared to the rate of formation of ethylene when only the longer wavelengths are absorbed by ethyl formate.

Runs 16 and 17 were done with the same experimental setup and at the same intensity as experiment 14. From the results of these experiments it follows that the rates of formation of carbon monoxide and hydrogen are practically independent of temperature, while the rate of formation of ethylene decreases with decrease in temperature. Runs 3, 4, and 5 of Table I lead to the same observation.

In the same table results are presented of runs where only the intensity has been varied. It can be seen that the carbon monoxide, hydrogen, and ethylene yields as well as the ratio  $C_2H_4/CO$  change only slightly, while the carbon dioxide and ethane yields increase markedly with diminishing intensities.

The results of the gas phase runs given in Table II indicate that addition of iodine does not affect the rate of formation of ethylene to any appreciable extent, while the rates of formation of methane, propane, and butane were reduced to negligible amounts. Increase of the temperature increases the rate of formation of the products with the exception of ethylene.

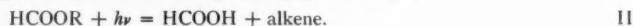
### Discussion

The results of Tables I and II indicate that the following intramolecular process occurs:



The independence with respect to temperature variation of the rate of formation of carbon monoxide over a temperature range from  $-80^\circ$  to  $13^\circ$  C. and over a large intensity range is good evidence for the occurrence of this process. The small increase of the hydrogen and carbon monoxide yields at high temperatures and low intensities may be attributed to a thermal decomposition of formyl radicals. The fact that the less stable acetyl radicals formed in the liquid phase photolysis of methyl and ethyl acetate decompose only to a small extent agrees with the proposition that at low temperatures carbon monoxide is formed mostly by process I.

Formates with a  $\beta$ -hydrogen may also decompose by process II:



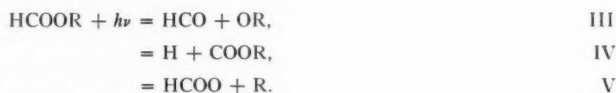
The following facts may be cited as evidence in favor of process II:

- (a) the independence of the ethylene yield in the liquid phase photolysis of ethyl formate over a considerable intensity range,
- (b) the only slight variation of the rate of formation of the alkenes with temperature,
- (c) the rate of formation of ethylene which in the gas phase photolysis of ethyl formate is unchanged upon addition of iodine.

It may be mentioned that pyrolysis studies (5) of several formates by the toluene carrier technique showed that formates with a  $\beta$ -hydrogen decompose by a molecular elimination process analogous to process II. Acetic anhydride may be cited as another example of the same type where photolysis (1) and pyrolysis (8) produce ketene and acetic acid in a direct process.

The ethyl formate results show that process I occurs mostly at wavelengths shorter than are required for process II. This indicates that processes I and II probably occur from different electronic levels.

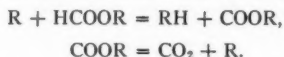
Besides the intramolecular processes one or more of the following dissociative steps has to occur:



From our results little can be said about the occurrence of these processes. Analogy with the liquid phase photolysis of the acetates and propionates favors processes III and IV.

Recent studies (6) on the gas phase photolysis of acetone in the presence of methyl formate have shown that methyl radicals only abstract the hydrogen atom from the

acyl group. One carbon dioxide molecule was found for every hydrogen abstracted. In agreement with this, the pronounced increase of the rate of formation of carbon dioxide and the corresponding hydrogen with increase in temperature and diminishing intensities can be explained by the following chain propagating steps:



The initiator may be any of the radicals formed in processes III, IV, and V.

Considering the primary processes mentioned above, hydrogen can at low temperatures only be produced by a reaction of the hydrogen atoms formed in process IV with other radicals present in the system or with formate molecules. It is perhaps surprising that the ratio  $\text{H}_2/\text{CO}$  is approximately the same for all runs done with the same lamp and at the same wavelength distribution.

It may be pointed out that at these wavelengths, hydrogen atoms cannot be formed by a primary process in which a hydrogen atom is split off from the alkyl group. This is substantiated by the fact that no hydrogen was found in the gas or liquid phase photolysis of the esters to be discussed later in this paper.

The methane and propane formed in the gas phase photolysis of ethyl formate indicate that even at room temperature the ethoxy radicals decompose to an appreciable extent into a methyl radical and formaldehyde.

## PART II. THE PHOTOLYSIS OF ESTERS OTHER THAN FORMATES

### Results

#### *Liquid Phase*

The results of the liquid phase photolysis of a few simple alkyl esters at varying temperatures and intensities have been summarized in Table III.

Only the volatile products have been determined quantitatively. In a few runs however some of the products were present in amounts too small to be measured with any accuracy. Except when stated otherwise, the incident intensity was the same as for the experiments given in Table I. For the runs where the intensity has been changed, the incident intensity is given relative to the constant intensity experiments. All the rates are expressed in  $\text{cc./min.} \times 10^4$ .

A few general features are as follows:

(a) Ethyl acetate and ethyl propionate give ethylene as an important product. The ethylene quantum yields are virtually not affected by a change in intensity.

(b) Propylene is the main volatile product in the photolysis of isopropyl and *n*-propyl acetate.

(c) In the photolysis of methyl *n*-butyrate a considerable amount of ethylene has been found.

(d) Some ethylene is also formed in the photolysis of methyl propionate. However, the rate of formation is only 10% of the rate of ethylene production in the photolysis of ethyl propionate.

(e) For most of these compounds a change in temperature produces a slight variation in the yields of the alkenes.

(f) All esters have carbon monoxide and carbon dioxide as products. The rates of formation of both compounds increase with temperature. The acetates produce less carbon monoxide, carbon dioxide, and hydrocarbons than the propionates and the butyrate.

TABLE III  
 LIQUID PHASE PHOTOLYSIS OF ESTERS

	Run	Temp., ° C.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_2H_6}$	$R_{C_3H_8}$	$R_{C_4H_{10}}$
Methyl acetate	a24	5	85	7.3	2.47	8.80	1.42		
	a25	29	55	11.8	7.80	12.0	1.80		
	Run	Temp., ° C.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_2H_6}$	$R_{C_3H_8}$	$R_{C_4H_{10}}$
Methyl propionate	a26	5	8	6.10	38.6	27.0	135	20.5	5.20
	a27	31	7	12.8	154	105	248	6.4	8.35
	a28	50	6	26.6	245	216	278	5.10	8.60
	a29	70	5	57.5	292	258	328	4.30	4.30
	Relative intensity 0.125								
	a30	5	35	0.75	7.45	6.82	26.7	2.30	
	a31	30	35	1.50	21.0	22.0	38.2	1.70	
	a32	50	30	4.45	36.5	34.5	45.8		
	a33	70	30	8.80	34.0	36.6	46.0		
	Run	Temp., ° C.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_3H_8}$	$R_{C_2H_6}$	$R_{C_2H_4}$
Methyl <i>n</i> -butyrate	a34	5	8	2.90	9.50	6.55	30.5	3.05	203
	a35	36	8	9.53	45.0	38.4	100	4.20	176
	a36	85	7	66.0	155	140	192		101
	Run	Temp., ° C.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_2H_6}$	$R_{C_3H_8}$	$R_{C_2H_4}$
Ethyl acetate	a37	3	5	1.1		1.0			255
	a38	30	4	4.3	3.8	4.0			260
	a39	70	4	20.5	25.5	14.0	15.0		238
Relative intensity 0.21									
	a40	3	122	0.34	0.90	0.30			46.0
	a41	26	37	1.10	2.25	0.80			55.8
	a42	52	41	2.80	3.15	2.05	2.70		58.0
	a43	74	20	4.75	5.40	4.40	4.00		47.0
	Run	Temp., ° C.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{C_4H_{10}}$	
Ethyl propionate	a44	4	4	8.40	33.2	71.0	200		34.4
	a45	30	3	20.5	85.0	130	176		25.0
	a46	30	4	19.0	87.0	135	181		22.0
	a47	50	3	36.0	155	227	168		19.5
	a48	70	3	59.2	186	315	155		16.0
	a49	90	3	83.5	198	384	136		10.0
	Relative intensity 0.125								
	a50	3	40	0.81	5.90	12.6	22.0		0.60
	a51	30	35	2.80	12.8	23.7	19.0		0.80
	a52	61	30	7.80	21.3	42.0	18.0		
	a53	90	30	13.0	23.5	51.0	18.0		
Relative intensity 0.0023									
	a54	30	1035	0.06	0.227	0.49	0.315		
	Run	Temp., ° C.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_3H_8}$	$R_{C_4H_{10}}$	
Isopropyl acetate	a55	7	6	0.40		0.50			370
	a56	31	6	1.40		2.60			319
	a57	77	6	16.0	15.0	18.0	18.5		255
<i>n</i> -Propyl acetate	a58	28	6	2.70		1.54			180
	a59	75	6	26.5	20.0	16.0	21.2		198

(g) In the photolysis of methyl and ethyl propionate, the rates of formation of carbon dioxide, methane, and ethane approach constant values at high temperatures. A decrease in intensity results in an increase of the yields of these three products. The results of the methyl propionate experiments indicate that at low intensities the rates of formation of carbon dioxide and methane are equal, while at high intensities the rate of formation of methane is somewhat less than that of carbon dioxide.

(h) Ethers were found to be present in the liquid phase photolysis of all the esters but their rates of formation were too small to be measured with any accuracy.

#### Gas Phase

Table IV represents the results of a few gas phase experiments. The incident intensity

TABLE IV  
GAS PHASE PHOTOLYSIS OF ESTERS

	Run	Temp., ° C.	Pres- sure, cm.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_2H_6}$				
Methyl acetate	a60	27	6.4	35	13.8	8.30	1.93	5.50				
	a61	120	8.35	25	73.2	16.7	7.00	33.8				
	a62	177	9.50	25	74.8	16.1	17.3	26.2				
	Run	Temp., ° C.	Pres- sure, cm.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{C_3H_8}$	$R_{C_4H_{10}}$	
Methyl propionate	a63	34	7.1	30	50.8	12.4	1.89	8.4	3.69	6.73	13.82	
	a64	124	9.1	25	59.0	13.4	3.95	11.0	4.10	8.40	12.40	
	a65	196	8.8	25	56.8	13.4	8.12	21.1	3.42	3.95	7.03	
	a66	1	1.8	40	19.2	6.90	0.79	4.02	1.80	2.86	7.10	
	a67	37	2.05	25	45.0	11.6	1.13	8.59	3.75	6.70	15.2	
	Run	Temp., ° C.	Pres- sure, cm.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{C_3H_8}$	$R_{C_4H_{10}}$	
Methyl <i>n</i> -butyrate	b68	29	2.85	25	55.0	15.3	1.40	1.7	4.65	3.25	9.10	
	a69*	29	3.0	800	0.43	0.415	0.043	0.05	0.13	0.029	0.089	
	Run	Temp., ° C.	Pres- sure, cm.	Time, min.	$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{C_3H_8}$	$R_{C_4H_{10}}$	$\frac{R_{C_2H_4}}{R_{CO_2}}$
Ethyl acetate	b70	-23	0.45	60	0.34	0.80	0.076	0.17	3.00	0.20	0.1	3.75
	b71	0	1.95	43	4.1	7.90	0.82	2.80	12.6	1.65	0.6	1.60
	a72	34	5.8	20	9.60	8.95	1.06	3.26	9.80	2.49	0.54	1.10
	a73	124	7.5	15	45.0	16.5	8.55	23.0	11.2	14.8	0.57	0.68
	a74	195	8.8	15	54.5	18.0	35.4	13.8	12.6	7.2		0.70
Ethyl propionate	a75	34	3.8	35	25.0	8.75	0.30	5.80	7.05	1.26	12.8	0.81
	b76†	30	3.3	1340	2.1	0.76	0.015	0.312	0.573	0.055	0.775	0.755
	b77*	30	3.3	1140	0.59	0.445	0.01	0.14	0.325	0.032	0.42	0.73
	Iodine present				$R_{CO}$	$R_{CO_2}$	$R_{CH_4}$	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{C_3H_8}$	$R_{C_4H_{10}}$	
Ester-iodine mixtures.—Temperature: 28° C. Ester pressure: 2.7 cm. Iodine pressure: 0.035 cm.												
$C_2H_5COOCH_3$	No	130	34.0	5.2	22.5	9.60	18.0	36.5				
	Yes	46.5	32.5	—	—	2.00	—	—				
$C_2H_5COOC_2H_5$	No	90.0	33.7	0.65	17.3	29.2	3.2	41.3				
	Yes	23.6	33.4	—	—	23.4	—	—				
$CH_3COOC_2H_5$	No	34.0	29.0	3.3	11.0	37.0	8.5	2.1				
	Yes	10.0	24.0	—	—	35.0	—	—				

\*Experiments carried out with Corning filter 9863.

†Experiment carried out at  $I_{rel} = 0.084$ .

was kept the same for all experiments done with mercury arc *a*. Except for runs 69, 76, and 77, the incident intensity has been kept constant for the runs performed with lamp *b*.

It can be seen that at high temperatures and for unfiltered light, carbon monoxide is the main product for all the esters studied. Under these experimental conditions CO/CO<sub>2</sub> was found to be larger than 3. However, a Corning filter 9863 used in the photolysis of ethyl propionate and methyl *n*-butyrate brings this ratio close to unity, while the C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> ratio stays practically unchanged.

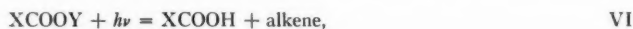
The results indicate that the rates of formation of carbon monoxide and carbon dioxide decrease appreciably with decrease in temperature. In the photolysis of ethyl acetate C<sub>2</sub>H<sub>4</sub>/CO<sub>2</sub> increases gradually with diminishing temperature. At -23° C. ethylene accounts for about 70% of the volatile products.

Addition of iodine to ethyl acetate and ethyl propionate causes only a slight decrease of the ethylene yield, while all the other hydrocarbons are reduced to trace amounts. In the photolysis of the methyl propionate - iodine mixture, the ethylene yield amounted to about 10% of the ethylene yield found in the photolysis of ethyl acetate and ethyl propionate. No other hydrocarbons were formed.

Except for the iodine mixtures, ethers were found in all runs but were not determined quantitatively.

#### Discussion

The results given in Tables III and IV indicate that the following intramolecular processes occur:



Y and X represent alkyl groups with respectively  $\beta$ - and  $\gamma$ -hydrogens.

In favor of process VI the following facts may be mentioned:

(a) At low temperatures ethylene is practically the only volatile product formed in both the gas and liquid phase photolysis of ethyl acetate. The other esters with a  $\beta$ -hydrogen in the alkoxy group have an alkene as major product. There is only slight variation with temperature of the rate of formation of the alkenes in the photolysis of these esters.

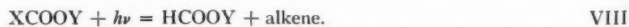
(b) In the liquid phase photolysis of ethyl acetate and ethyl propionate, the ethylene yields are independent of intensity.

(c) In the photolysis of the ethyl propionate - iodine mixture, ethylene is a major product. The decrease of the ethylene yield is probably due to the elimination of the following disproportionation reactions:



The existence of process VII is substantiated by the presence of ethylene as an important product in both the gas and liquid phase photolysis of methyl *n*-butyrate. This process is analogous to the intramolecular rearrangement which was found to occur in the photolysis of ketones and aldehydes with  $\gamma$ -hydrogens in the alkyl groups (7).

The small ethylene and propylene yields in the liquid phase photolysis of methyl propionate and methyl *n*-butyrate indicate that process VIII does not occur to any appreciable extent,



Also, a considerable fraction of the ethylene and propylene may be expected to be formed in disproportionation reactions between ethyl radicals and other radicals present.



However, the small amount of ethylene found in the gas phase photolysis of the methyl propionate-iodine mixture seems to indicate that process VIII might occur to some extent. In analogy with this, recent work (4) on the gas phase photolysis of propionaldehyde and *n*-butyraldehyde showed that at 2380 and 1870 Å, these two compounds decompose to some extent into formaldehyde and the corresponding alkene. It should be pointed out, however, that the iodine runs given in Table IV were performed with unfiltered light. This may have led to the formation of ethylene by a disproportionation between ethyl radicals and iodine atoms.

The low carbon monoxide yields in the low temperature gas and liquid phase photolysis of the acetates, the very small ether yields in the liquid phase photolysis of all the compounds studied, and the absence of ethers in the iodine experiments indicate that process IX does not occur,



#### Dissociation Processes

The following primary processes will be considered briefly:



The fact that for unfiltered light, carbon monoxide is the main product in the high temperature gas phase photolysis of all the esters indicates that under these experimental conditions process X is the most important one. It can be seen that the carbon monoxide yield for the high temperature gas phase runs is practically the same for all compounds and does not show any appreciable variation with temperature.

The decrease of the rate of formation of carbon monoxide with diminishing temperatures in both gas and liquid phase photolysis proves that only a small fraction of the XCO radicals decompose by the excess energy carried over from the primary process. In the iodine runs the CO yields are fairly high. However, it is possible that at these low iodine pressures a fraction of the XCO radicals decompose before reacting with iodine.

It is not possible to decide from the gas phase runs if the CO<sub>2</sub> comes from the decomposition of COOY, XCOO, or from both radicals:



Both radicals are considered to be fairly unstable at room temperature. However, at low temperatures the CO<sub>2</sub> yield decreases appreciably in both the gas and liquid phase photolysis. Although no conclusive evidence can be given, the following facts indicate that reaction *b* and consequently process XI is the most likely one to occur:

1. The rates of formation of methane and carbon dioxide in the liquid phase photolysis of methyl propionate are equal at low intensities and at all temperatures. Recombination of methyl radicals with other radicals present in the system explains the somewhat lower methane yields in the high intensity runs. The results of the liquid phase photolysis of methyl *n*-butyrate lead to the same conclusion.

2. At low temperatures  $(\text{C}_2\text{H}_6 + 2\text{C}_4\text{H}_{10} + \text{C}_3\text{H}_8)/(\text{CO} + \text{CO}_2)$  is much larger than unity in the liquid phase photolysis of methyl propionate, while  $\text{C}_3\text{H}_8 > (\text{CO}_2 + \text{CO})$  in the photolysis of methyl *n*-butyrate. This proves that there are COOY radicals formed which react with other species instead of decomposing.

However, the fact that the carbon dioxide yields are considerably lower for the acetates than for the propionates and butyrates remains unexplained. On the assumption that the  $\text{CH}_3\text{CO}_2$  radicals are more stable than the  $\text{C}_2\text{H}_5\text{CO}_2$  or  $\text{C}_3\text{H}_7\text{CO}_2$  radicals, this observation would rather tend to favor process XII.

Cutting off short wavelengths in the gas phase photolysis of ethyl propionate and methyl *n*-butyrate reduces considerably the carbon monoxide yield as compared to the ethylene and carbon dioxide yields. This proves that process X occurs at shorter wavelengths than processes VI, VII, and XI.

After subtracting the amounts of ethylene formed in reaction [1], values of 0.66, 0.64, and 0.63 can be obtained for the ratio  $\text{C}_2\text{H}_4/\text{CO}_2$  in the gas phase ethyl propionate runs *a75*, *b76*, and *b77*. The ethyl propionate - iodine run indicates that the contribution of reaction [2] is small. In the gas phase photolysis of methyl *n*-butyrate, values of 0.304 and 0.303 were obtained for the ratio  $\text{C}_2\text{H}_4/\text{CO}_2$  in experiments *b68* and *b69*. From the independence of the  $\text{C}_2\text{H}_4/\text{CO}_2$  rates with change in wavelength, it may be concluded that processes VI and XI on the one side, and processes VII and XI on the other side, probably result from the same electronic level.

It can be seen that the value for the  $\text{C}_2\text{H}_4/\text{CO}_2$  ratio in the liquid phase photolysis of ethyl propionate at 90° C. and low intensity, under which conditions the  $\text{CO}_2$  yield attained a constant value, does not differ very much from the one found in the gas phase photolysis of this compound.

Summarizing the results, it may be concluded that processes I and X take place at short wavelengths, while the other intramolecular and dissociation processes occur at long wavelengths as well. In a later publication (3) it will be shown that addition of certain solvents leaves processes I and X unaffected, while the others are strongly suppressed.

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# TREATMENT OF EXPERIMENTAL DATA IN THE STUDY OF CHELATION<sup>1</sup>

G. F. ATKINSON AND W. A. E. MCBRYDE

## ABSTRACT

Calculation from experimental formation constants of the various species of metal chelates that predominate for a given system under different experimental conditions is facilitated by the use of a digital computer. A convenient graphical representation of the results obtained in this way is proposed. From the plotted data one may select conditions for a photometric analytical procedure that will ensure the exclusive formation of a single chelate species. The changes in species that accompany changes in pH for some systems introduce a variable and appreciable contribution to the ionic strength of the solution, the magnitude of which may be estimated from the results of the foregoing calculation.

## USE OF A DIGITAL COMPUTER

Many methods of attacking the problem of the stoichiometry and stability of metal chelate complexes have been reported in the literature (1, 2, 3, 4, 5). These give rise to sets of values for

$p$  = number of ligand groups attached,  
 $K$  = formation constant(s),

at particular values of

$r$  = molar ratio of reagent to metal,  
 $[M]_T$  = metal concentration put in.

The choice of experimental conditions by each investigator often seems rather arbitrary.

Clearly, it is advantageous for the analytical chemist to survey the behavior of a chelate system over a range of pH and  $r$ , rather than to devise an empirical procedure closely based on the conditions of the original study. Not only may it be possible to economize on the consumption of frequently expensive reagents, but also it may be possible to arrive at an estimate of the precision needed in reproducing conditions (buffering, etc.) in successive determinations. Unfortunately, because of the number of equilibria involved in forming chelate complexes in aqueous solutions, the determination of the probable solution constituents involves exceedingly tedious calculations, and is seldom undertaken.

We have sought to reduce the labor of calculation by making use of the University of Toronto's electronic digital computer "FERUT".

The chelate system selected was iron(III) plus tiron (4,5-dihydroxybenzene-1,3-disulphonic acid). We shall employ the abbreviated formula  $H_4Bz$  for tiron, following Schwarzenbach (6). This system presents more than usual complexity for computation because of the presence in acidic solutions of both protonated and unprotonated 1:1 complexes (6). It was further felt to be an appropriate choice since  $K$  values determined for  $r = 3$  and for  $r = 6.4$  are in fair agreement with each other (7). Schwarzenbach's values for  $K$  were used for the calculation.

## The Equations

Iron(III) is distributed according to

$$[1] \quad [Fe]_T = [Fe_0] + [FeBz] + [FeBz_2] + [FeBz_3] + [FeHBz],$$

where  $[Fe]_T$  = stoichiometric concentration of iron put in,

$Fe_0$  = all species not involving tiron,

$Bz$  = "tironate" ion,  $C_6H_2(SO_3)_2O_2^{-4}$ .

<sup>1</sup>Manuscript received October 17, 1957.

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario.

Tiron is distributed among the four species with iron as above, and also among Bz, HBz, and H<sub>2</sub>Bz. So when iron is not present

$$[2] \quad [T]_T = [T_F] = [Bz] + [HBz] + [H_2Bz]$$

and when iron is present

$$[3] \quad \begin{aligned} [T]_T &= [T_F] + [T_C] \\ &= [Bz] + [HBz] + [H_2Bz] + [FeBz] + 2[FeBz_2] + 3[FeBz_3] + [FeHBz], \end{aligned}$$

where

$[T]_T$  = stoichiometric concentration of tiron put in,  
 $T_F$  = tiron not in species with iron,  
 $T_C$  = tiron in species with iron.

Using the expressions defined by Schwarzenbach and Willi (6) for the equilibrium constants, we may set up the following equations:

$$[4] \quad [Bz]/[T]_T = 1/(1 + K_1[H] + K_1K_2[H]^2) \equiv \alpha,$$

$$[5] \quad [HBz]/[T]_T = (1 - \alpha)/(1 + K_1[H]) \equiv \beta,$$

$$[6] \quad [H_2Bz]/[T]_T = 1 - (\alpha + \beta),$$

$$[7] \quad \begin{aligned} [Fe_0]/[Fe]_T &= 1/(1 + K_3[Bz] + \alpha^2 K_3 K_4 [Bz]^2 + \alpha^3 K_3 K_4 K_5 [Bz]^3 + K_7[Bz]) \\ &\equiv C_0, \end{aligned}$$

$$[8] \quad \begin{aligned} [FeBz]/[Fe]_T &= (1 - C_0)/(1 + \alpha K_4[Bz] + \alpha^2 K_4 K_5 [Bz]^2 + K_6[H]) \\ &\equiv C_1, \end{aligned}$$

$$[9] \quad \begin{aligned} [FeBz_2]/[Fe]_T &= \{1 - (C_0 + C_1)\} / \{1 + \alpha K_5[Bz] + K_6[H]/\alpha K_4[Bz]\} \\ &\equiv C_2, \end{aligned}$$

$$[10] \quad [FeBz_3]/[Fe]_T = \{1 - (C_0 + C_1 + C_2)\} / \{1 + K_6[H]/\alpha^2 K_4 K_5 [Bz]^2\} \equiv C_3,$$

$$[11] \quad [FeHBz]/[Fe]_T = 1 - (C_0 + C_1 + C_2 + C_3) \equiv C_4.$$

#### The Calculations

The computer program was devised to evaluate these equations systematically at regularly spaced values of [Bz], pH, and [Fe]<sub>T</sub>. Sets of values having  $r < 1$ , and having  $[T]_T > 0.5$  molar were automatically discarded, thus limiting the output of results to a useful range. Output was presented as shown for each case:

[Bz]	pH	[Fe] <sub>T</sub>		
[T] <sub>F</sub>	[T] <sub>C</sub>	[T] <sub>T</sub>	[T] <sub>C</sub> /[T] <sub>T</sub>	
C <sub>0</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>

It should be pointed out that the application of this technique to all systems consisting of equivalent sets of complex species requires the writing of only one program for the computer, the various  $K$  values being supplied as number input in each application of the program. Furthermore it is apparent from the equations that minor modifications will enable the many *tris*-complex systems in which only three species are recognized (MR, MR<sub>2</sub>, and MR<sub>3</sub>) to be handled by the program.

#### PRESENTATION OF COMPUTED RESULTS

Various graphical methods of displaying the computed results are possible.

In dealing with the effect of pH on polybasic acids, the fraction of acid present in each ionic or molecular species is often plotted against pH (see, e.g., 8). Curves of this type for

several values of  $r$  are shown in Fig. 1. Their greatest usefulness is in the interpretation of experiments in which a property having a characteristic value for each species (e.g. optical absorption) is measured over a range of pH.

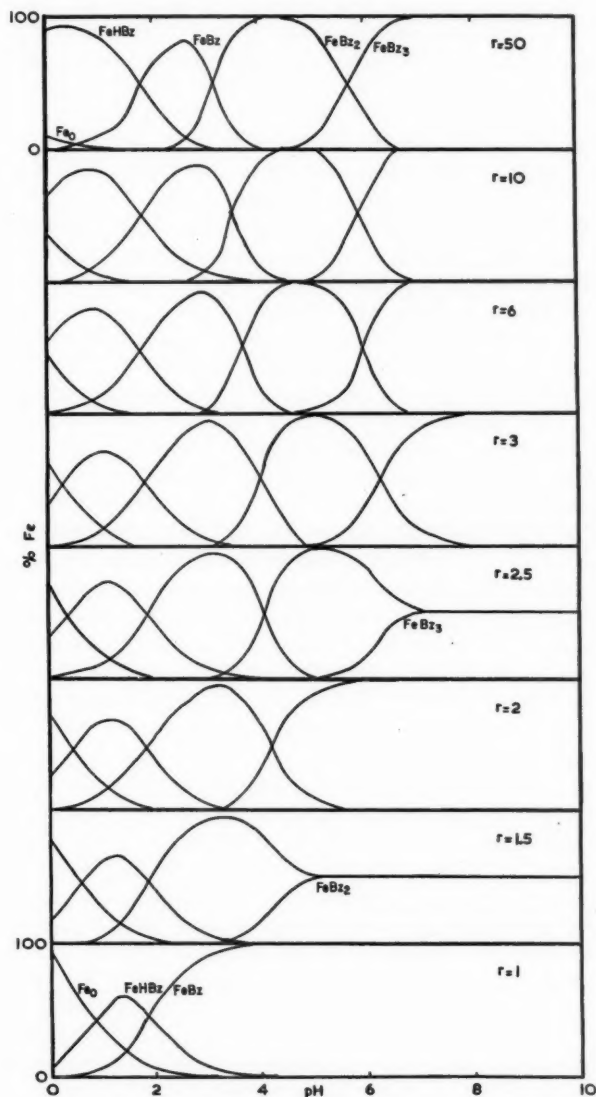


FIG. 1. Distribution of species according to pH.

Ågren (1), having drawn such diagrams with non-overlapping regions, proposes that the abscissae be made  $\text{pH} - \text{pRH}$  rather than pH, to permit the representation of conditions at more than one concentration of chelating agent.

We propose that such data may to advantage be represented as in Fig. 2(a), which

shows a contour map of fractions of species, plotted on axes of pH and  $\log r$ . The region of greatest occurrence of each species is designated by the formula; and contours showing the percentage distribution of iron among the several species are also drawn. In Fig. 2(b), on the same axes, are shown areas in which stated proportions of reagent are present as species with iron. Used together, such diagrams indicate the regions of greatest interest for the development of analytical procedures, and suggest the necessary precision of pH adjustment, etc., in such procedures.

It is not difficult from such a diagram to see why different authors have differently described the color of iron(III)-tiron solutions in the vicinity of pH 4. The maintenance of constant pH by buffering does not assure the presence of a single species, changes in solution composition occurring also with variation of  $r$ , and of ionic strength. It may be added that, as far as the authors have been able to determine, the species FeBz and FeHBz have identical absorption spectra, but in order to produce these species in equivalent concentrations from solutions possessing the same content of iron(III) it has been necessary to provide solutions of equal ionic strength.

The figures reproduced here are simplified by the plotting of very few contour lines in the interest of facile reproduction, but any desired smaller interval could be selected. If this is done, it is less confusing to plot the curves for each species on a separate diagram.

These diagrams, while providing a potentially useful analysis of the solution constituents in the iron(III)-tiron system, must be applied with some restraint. For one thing, in the calculations upon which they are based it has been assumed that values of  $K$  taken from experiments in which  $r = 3$  are valid for all values of  $r$ . In principle this assumption should be permissible, but it must be recalled that Freiser and co-workers have shown for *o*-aminophenol and for dimethylglyoxime that values of the apparent stability constants for certain metallic derivatives are *not* completely independent of values of  $r$  (9, 10). We therefore feel that, lacking evidence on this score, our values in the range  $r > 10$  should be regarded with less confidence than those in the range  $r < 10$ . Care must also be taken to confine application of the data within limits for which the postulated reactions are valid. Thus, to select  $r = 5$ , pH = 9, for the determination of iron as its 3:1 tiron complex may introduce difficulty because of air-oxidation of the reagent, in which case equation [3] is no longer valid.

Strictly speaking, precise knowledge of the distribution of ferric iron among several species in solution requires that account be taken also of the formation of complex ions with any other anions in solution, particularly of any buffer present, and of hydrolysis of the metallic ion. For the latter one might incorporate the data of Hedström (11) or of Milburn and Vosburgh (12) into the calculation. As far as making allowance for other species in solution is concerned, several difficulties arise: data for interaction of ferric iron with acetate or phthalate are apparently not available (13), but even if they were the manner of using them would be complicated by the probability of formation of mixed complexes with tiron; there would then have to be as many calculations of the distribution of species as there are buffer systems selected. The data of Fig. 2 are applicable to systems including other anions only if the assumption is made that the stability constants of species formed by ferric iron with the latter are very small compared with the formation constants of the tironate species. Furthermore, since Schwarzenbach measured the formation constants upon which our calculations are based in 0.1 *M* chloride solutions, any use of the results of the calculations for solutions of other concentrations of chloride requires the further assumption that the reaction of ferric iron with chloride is only slight compared to that with tiron. In this connection it may be recalled that Foley and Anderson described the effect of changing the buffering constituents on the formation of ferric



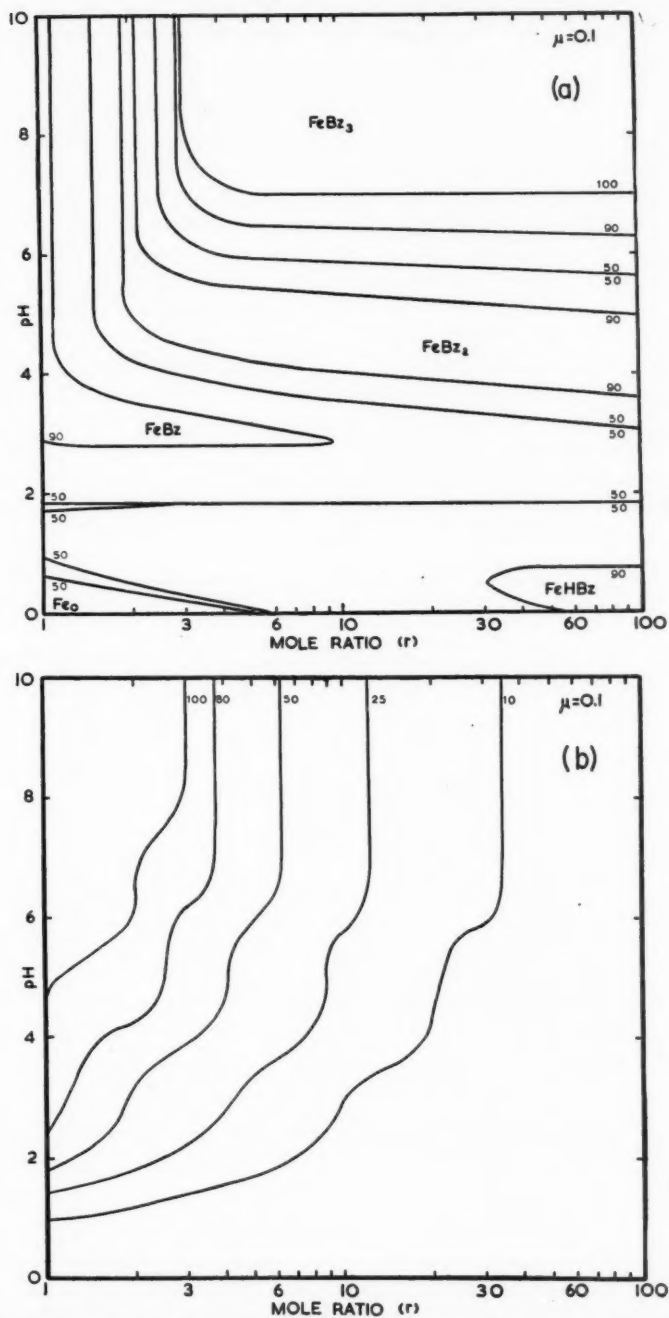


FIG. 2. Distribution of species according to pH and  $r$ ; (a) percentage of iron present in stated forms, (b) percentage of tiron bound to iron.

sulphosalicylate complexes (14). However, the interpretation of these results by these authors has not been borne out by the more complete investigations of Ågren (1) or Vareille (15).

#### EFFECT OF CHANGES IN pH ON IONIC STRENGTH

The authors are currently investigating the effect of changes in ionic strength upon the apparent equilibrium constants for this system, and consequently upon the distribution of metal among the various species. We have already observed in spectrophotometric measurements that this effect is considerable at low pH(16).

For our experiments it would be desirable to be able to work at values of the ionic strength low enough to deny to us the convenience of adding gross amounts of indifferent electrolyte, and thereby the need arises to know rather accurately the contributions to ionic strength of all species in solution. It is apparent that the large contribution of the highly charged chelate species (in this system) will vary markedly with pH. In a similar context Olson and Simonson (17) have shown that the effects of maintaining "constant concentration of inert electrolyte" and "constant ionic strength" are not the same when the species present are changing.

By means of Fig. 2 we have computed the total contribution of species arising from ferric perchlorate and tiron for values of  $r = 3, 10, \text{ and } 30$ . These results, plotted as  $\log \mu$  against pH, are shown in Fig. 3.

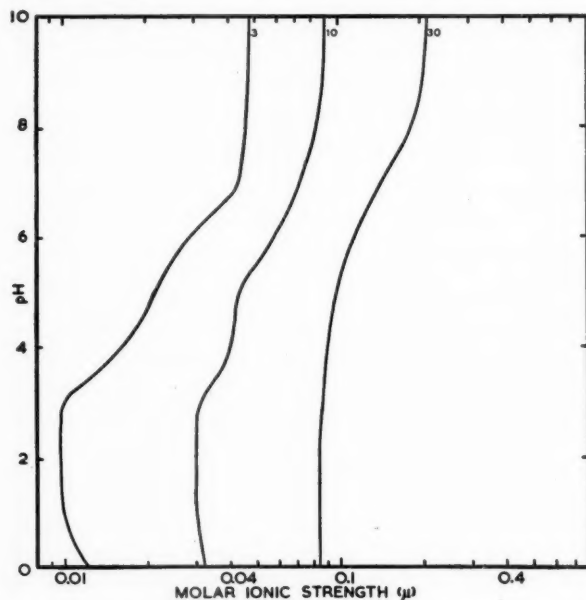


FIG. 3. Contribution to ionic strength of species from  $\text{Fe}(\text{ClO}_4)_3$  and tiron. Determinant variable of curves:  $r$ .

It may be noted that Schwarzenbach's values for  $K$  were determined with  $[\text{Fe}]_T = 1.11 \times 10^{-3} M$ ,  $r = 3$ , and a solution of nominal ionic strength  $0.1 M$  by addition of potassium chloride. It appears from our calculations that to this value must be added a

contribution from the several complex species amounting to as much as one-half of the nominal value, depending on pH. It follows that only in solutions of moderately high concentration of indifferent electrolyte (cf. Ågren (1)) will the ionic strength be relatively "constant" throughout the range of pH corresponding to the formation of the different complexes in this system.

#### ACKNOWLEDGMENT

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# THE LIQUID PHASE PHOTOLYSIS OF DIETHYL KETONE AND METHYL ETHYL KETONE<sup>1,2</sup>

P. AUSLOOS<sup>3</sup>

## ABSTRACT

The liquid phase photolysis of diethyl ketone has been studied in the temperature range from  $-35^{\circ}$  to  $95^{\circ}$  C. The CO quantum yield at  $95^{\circ}$  C. was found to be close to unity. At  $28^{\circ}$  C. decrease in intensity and addition of heptane led to a substantial increase of the CO and the ethane yields.

The methyl ethyl ketone liquid phase photolysis at temperatures between  $5^{\circ}$  and  $75^{\circ}$  C. led to the same observations. Arrhenius plots of  $R_E/R_B^{1/2}[K]$  gave for both compounds a value of 5 kcal./mole.

Gas phase studies in the temperature range of  $0^{\circ}$  to  $60^{\circ}$  C. confirmed the low CO quantum yield reported previously and showed evidence for disproportionation and recombination reactions between ethyl and propionyl radicals.

## EXPERIMENTAL

Eastman Kodak Company methyl ethyl ketone and diethyl ketone (white label) were distilled through 10 theoretical plates with rejection of large head and tail fractions. Air was removed by bulb-to-bulb distillation in the vacuum line.

Gas phase experiments were performed with a Hanovia (16A-13) SH type medium pressure lamp. The cylindrical quartz cell (5 cm. diameter, 10 cm. long) was completely filled with a nearly parallel light beam.

The liquids were irradiated in a quartz cell of 5 cm. diameter and 0.05 cm. depth. The cell was provided with two outlets, one of which was sealed after filling, while the other was closed by a break seal which made it possible to attach the cell to the analysis system after each experiment. Between runs the cell was washed out with diethyl ketone and dried at about  $150^{\circ}$  C. The irradiation was carried out in a thermostat consisting of a brass cylinder with evacuated double walls and double quartz windows. For experiments above room temperature an electric immersion heater was brought into distilled water, while for the low temperature experiments the thermostat was filled with methanol cooled by dry ice. In this way it was possible to maintain the temperature constant within half a degree.

At  $3130 \text{ \AA}$  about 98% of the incident radiation is absorbed by the undiluted ketone. In order to compensate for this sharp absorption decrease throughout the cell, two Hanovia lamps were placed opposite each other with the cell fixed in the center of the nearly parallel light beam.

Except for experiments 1 and 2 Corning filters (9-53) were used to cut off wavelengths below  $2800 \text{ \AA}$ . The incident intensity was varied by means of copper gratings.

After irradiation of the liquid the cell was attached to the analysis system, consisting of three traps and one modified Ward still. The  $\text{CO}-\text{CH}_4$  fraction was removed at solid nitrogen temperature and was analyzed by combustion over hot CuO. The  $\text{C}_2\text{H}_6-\text{C}_2\text{H}_4$  fraction was taken off at  $-160^{\circ}$  C.  $\text{C}_2\text{H}_4$  was determined by hydrogenation over a Ni

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catalyst (16). The  $C_4H_{10}$  fraction was separated at about  $-120^\circ\text{C}$ . In view of the high  $C_2H_6/C_4H_{10}$  ratio, which in some experiments was higher than 100, great care was taken that no ethane was left over from the previous distillation.

## RESULTS

*Gas Phase*

Table I represents the data of experiments performed at approximately constant diethyl ketone concentration. Runs 1 and 2 were done with an unfiltered light beam and at constant intensity. The other runs were performed with a Corning filter 9-53 and constant incident light intensity.

TABLE I  
GAS PHASE PHOTOLYSIS OF DIETHYL KETONE

Run	Temp., ° C.	Time, min.	Pressure, molec./cc. $\cdot 10^{-17}$	$R_{CO}$	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{C_4H_{10}}$	$C_2H_4/C_4H_{10}$	$C_2H_6/C_4H_{10}$	M.B.
Unfiltered light										
1	0	10	2.45	51.0	11.2	11.4	72.3	0.155	0.157	1.64
2	57	10	2.45	220.0	23.4	26.5	194.0	0.120	0.136	1.00
Corning filter 9-53										
3	0	8	2.42	13.05	2.97	3.15	17.9	0.166	0.176	1.60
4	13	12	2.48	27.0	4.27	4.60	28.5	0.149	0.162	1.22
5	25	12	2.46	43.8	5.29	5.95	41.2	0.128	0.144	1.07
6	60	12	2.45	54.8	5.50	6.98	46.4	0.119	0.150	0.96
7*	25	12	2.43	2.12	<0.1	<0.1	0.1			

\*Iodine added.

It can be seen that in both series of experiments the rates of formation of all the products decrease with temperature. In the last column M.B. stands for the material balance  $[\frac{1}{2}(C_2H_4 + C_2H_6) + C_4H_{10}]/CO$ . This ratio increases appreciably with decrease in temperature.

*Liquid Phase*

All experiments given in Tables II and IV and runs 36, 39, 40, 44, 45 of Table V were conducted at the same incident intensity.

Table II shows the results of experiments done in a temperature range from  $-35^\circ$

TABLE II  
LIQUID PHASE PHOTOLYSIS OF DIETHYL KETONE  
Variation of rate with temperature

Run	Temp., ° C.	Time, min.	$R_{CO}$	$R_{C_2H_4}$	$R_{C_2H_6}$	$R_{C_4H_{10}}$	$R_E/R_B^{\frac{1}{2}} \cdot 10^{-8}$
molec./cc./sec. $\cdot 10^{-15}$							
8	-35	8	0.20	1.05	4.30	0.54	1.86
9	-14	8	0.58	1.40	11.6	0.75	4.25
10	5	6	1.26	1.62	26.0	1.02	8.20
11	28	4	4.10	3.40	70.0	2.21	14.9
12	51	4	22.0	2.73	111	1.80	26.0
13	72	2	52.0	2.07	145	1.26	40.8
14	84	2	63.0	1.91	146	0.90	48.5
15	86	2	64.2	1.58	149	0.82	52.0
16	94	2	70.0	1.25	152	0.55	65.0

Acetone at  $28^\circ\text{C}$ :  $R_{CO}$ , 0.15;  $R_{CH_4}$ , 3.20;  $R_{C_2H_6}$ , 0.078.

to 94° C. It can be seen that the rates of formation of carbon monoxide and ethane both increase with temperature. At higher temperatures they approach constant values.

A rough measure of the quantum yield was obtained by comparing the rate of formation of carbon monoxide from the gas phase photolysis of diethyl ketone at 95° C. with the rate of formation from the liquid phase photolysis at the same temperature. The measurements were done with Corning filter 9-53 and cells of respectively 5 and 0.05 cm. depth. On the assumption that the quantum yield for CO in the vapor phase was unity, it was found that approximately  $8 \times 10^{16}$  quanta per second were absorbed by the liquid. This led to  $\phi(\text{CO}) \sim 0.87$  at 95° C.

The rates of formation of ethylene and butane show a pronounced increase with temperature up to 28° C. followed by a gradual decrease.

In the same table are included the results of one acetone liquid phase experiment, performed at 28° C. and under the same experimental conditions as the previous runs. Comparison with the diethyl ketone results leads to a CO quantum yield roughly equal to  $2 \times 10^{-3}$ . This figure is somewhat higher than previous estimates (11, 15).

In Table III the results of experiments carried out at 5°, 28°, and 84° C. and at various intensities are shown.  $I_{\text{rel}}$  represents the incident intensity relative to the highest intensity run. Values of  $R_{\text{C}_2\text{H}_6}/I_{\text{rel}}$  given in the last column show an increase with decrease in intensity. It can be seen from the data that this trend is even more pronounced for  $R_{\text{CO}}/I_{\text{rel}}$ . These results indicate clearly that the CO and ethane yields increase with diminishing intensity. However, this increase is much smaller at 84° C. where the quantum yield is already close to unity.

TABLE III  
LIQUID PHASE PHOTOLYSIS OF DIETHYL KETONE  
Variation of rate with intensity

Run	$I_{\text{rel}}$	Time, min.	$R_{\text{CO}}$	$R_{\text{C}_2\text{H}_4}$	$R_{\text{C}_2\text{H}_6}$	$R_{\text{C}_4\text{H}_{10}}$	$R_{\text{E}}/R_{\text{B}} \cdot 10^{-3}$	$R_{\text{E}}/I_{\text{rel}}$
At 28° C.								
17	1	6	3.87	3.15	70.1	2.25	14.8	70.1
18	0.410	10	2.11	1.15	35.5	0.59	14.6	86.5
19	0.354	15	1.66	0.80	28.1	0.435	13.5	79.8
20	0.354	15	1.72	0.79	28.0	0.42	13.6	79.5
21	0.125	35	0.82	0.21	11.7	0.090	12.3	93.5
22	0.044	100	0.49	0.045	4.25	0.014	11.2	96.5
23	0.0055	800	0.19	0.003	0.75	$\sim 0.0009$	$\sim 8.00$	136.0
At 5° C.								
24	1	10	1.24	1.59	26.1	1.06	8.00	26.1
25	0.354	30	0.39	0.54	11.9	0.235	7.80	33.7
26	0.125	90	0.20	0.225	6.52	0.09	6.80	52.2
At 84° C.								
46	1	4	62.2	1.85	147.0	—	—	147
47	0.0067	504	0.0512	$0.18 \times 10^{-3}$	0.103	—	—	154

In Table IV are given results of experiments made at 28° C. with *n*-heptane and *n*-octane as solvents. In the second column the percentage of light absorbed by the liquid has been given. Absorption measurements were made with a Cary absorption spectrophotometer. From the data it follows that the ratios  $R_{\text{C}_2\text{H}_6}/I_{\text{abs}}$  and  $R_{\text{CO}}/I_{\text{abs}}$  increase with dilution.



TABLE IV  
 LIQUID PHASE PHOTOLYSIS OF DIETHYL KETONE HYDROCARBON MIXTURES AT 28° C.

Run	$I_{\text{abs}}$	Time, min.	Heptane molec./cc. $10^{-21}$	DK molec./cc. $10^{-21}$	$R_{\text{CO}}$	$R_{\text{C}_2\text{H}_4}$	$R_{\text{C}_2\text{H}_6}$	$R_{\text{C}_4\text{H}_{10}}$	$R_E/R_B^{\dagger} \cdot 10^{-8}$
27	95%	6	1.36	3.85	5.75	4.95	67.5	3.37	11.6
28		6	2.03	2.84	5.20	5.10	53.0	3.72	8.70
29		6	3.05	1.42	5.27	3.15	32.2	2.40	6.60
30		6	3.25	1.14	4.85	2.80	25.3	2.14	5.50
31	22%	6	3.55	0.71	4.36	2.70	19.0	2.00	4.25
32		6	3.70	0.515	3.60	2.22	14.8	1.70	3.60
33	8.5%	6	3.88	0.27	2.82	1.96	10.8	1.04	3.35
34		6	2.67*	1.14	4.40	4.00	32.5	2.76	6.18
35		6	3.25*	0.515	3.43	3.82	18.9	2.75	3.60

\*Octane.

In Table V are given the results of the liquid phase photochemical decomposition of methyl ethyl ketone. The experiments were done in the temperature range from 5° to 70° C. and at varying intensities. The rates of formation of carbon monoxide, methane, ethylene, ethane, and butane have been measured. Although propane was present, it could not be determined with any accuracy because it was present in an amount less than 1% of the ethane fraction.

 TABLE V  
 LIQUID PHASE PHOTOLYSIS OF METHYL ETHYL KETONE  
 Variation of rate with temperature and intensity

Run	$I_{\text{rel}}$	Time, min.	Temp., ° C.	$R_{\text{CO}}$	$R_{\text{CH}_4}$	$R_{\text{C}_2\text{H}_4}$	$R_{\text{C}_2\text{H}_6}$	$R_{\text{C}_4\text{H}_{10}}$	$R_E/R_B^{\dagger} \cdot 10^{-8}$
36	1	10	6	0.54	0.88	1.70	17.2	1.12	5.15
37	0.354	30	6	0.18	0.215	0.310	7.70	0.225	5.15
38	0.125	80	6	0.028	0.036	0.076	3.20	0.039	5.10
39	1	10	23	1.66	2.05	1.93	34.0	1.46	9.22
40	1	10	26	1.76	2.42	2.17	38.2	1.65	9.40
41	0.354	30	26	0.50	0.85	0.62	17.2	0.35	9.20
42	0.125	80	26	0.10	0.15	0.115	6.30	0.070	7.50
43	0.125	80	26	0.089	0.122	0.080	5.95	0.050	8.40
44	1	10	45	3.20	4.05	1.56	49.5	1.14	14.6
45	1	8	70	7.00	7.60	1.01	59.2	0.56	24.8

Comparison of the runs at constant intensity at varying temperatures shows that the rates of formation of carbon monoxide, methane, and ethane increase with temperature. However, the increase of the rate of formation of ethane is less pronounced at higher temperatures, where it reaches a value close to one half the value found in the liquid phase photolysis of diethyl ketone under the same experimental conditions.

The ratios  $\text{C}_2\text{H}_4/\text{C}_4\text{H}_{10}$  do not differ very much from those found in the diethyl ketone photolysis. The rates of formation of ethane and butane both go through a maximum around 28° C. Decrease of intensity leads to a substantial decrease in the CO,  $\text{C}_2\text{H}_4$ , and  $\text{C}_4\text{H}_{10}$  yields, while the  $\text{C}_2\text{H}_6$  yields increase slightly.

## DISCUSSION

*Diethyl Ketone**(a) Gas Phase*

The gas phase photolysis of diethyl ketone has been extensively investigated in the past (8, 9, 10, 13).

In the course of this work a few runs were performed at low temperatures in order to obtain additional information about the primary process and reactions involving the propionyl radical.

The results given in Table I indicate that at relatively high intensities, the quantum yield of the CO production drops appreciably at temperatures below 60° C. A value of 0.23 can be estimated for the CO quantum yield at 0° C., if at 60° C. the quantum yield is assumed to be 1. These results are in agreement with earlier work (13), where at 25° C. and comparable intensities a value of 0.6 was found for the quantum yield of the CO formation.

The low CO quantum yield suggests as main primary process:

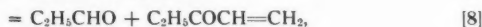
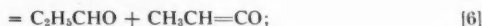


in which the propionyl radical may eventually decompose by excess energy carried over from the primary process or by thermal reaction:



Assuming that no collisional deactivation of the excited diethyl ketone molecules occurs, run 7 as well as recent work on the photooxidation of diethyl ketone (12) suggests that at most 5% of the propionyl radicals decompose as a result of the primary process.

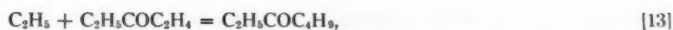
Besides decomposing, the propionyl radical may react with other species. Several combination and disproportionation reactions involving the propionyl radical may occur:



The increase of the  $\text{C}_2\text{H}_4/\text{C}_4\text{H}_{10}$  and  $\text{C}_2\text{H}_6/\text{C}_4\text{H}_{10}$  ratios with diminishing temperatures may be considered as good evidence for the occurrence of the reactions [3] and [4], while the fact that  $(\text{C}_4\text{H}_{10} + \frac{1}{2}\text{C}_2\text{H}_4 + \frac{1}{2}\text{C}_2\text{H}_6)/\text{CO}$  becomes larger than unity at low temperatures substantiates reaction [5] and perhaps also reaction [6]. Although there is no direct evidence for reactions [7], [8], and [9], it is quite likely, in view of their exothermicity, that these reactions occur.

Ethyl radicals disappear mainly by reactions [2], [3], [4], or by one of the following reactions:





Gas phase studies led to a value of  $0.12 \pm 0.01$  for  $k_{12}/k_{11}$  (2, 8, 13), while  $E_{10} - \frac{1}{2}E_{11}$  was found to vary from 7.5 to 9 kcal./mole depending on the temperature range (3, 8, 13).

At the temperatures used in this work the pentanonyl radical does not decompose to any appreciable extent and will eventually disappear by a radical reaction such as [7], [8], [9], [13], [14], [15] or by one of the following reactions:



#### (b) Liquid Phase

##### Primary process

From the results given in Table II it follows that the carbon monoxide and ethane yields approach constant values at high temperatures, which correspond to a primary quantum yield close to unity.

The fact that at room temperature the carbon monoxide yield increases appreciably with diminishing intensity and increasing dilution may be considered as evidence for a competition between reaction [1] and the radical reactions involving the propionyl radical. It is likely that infinite dilution at these temperatures may lead to a primary quantum yield equal to one.

The quantum yield determination at 95° C. is not accurate enough to decide whether any primary or secondary diffusive recombination occurs. If any recombination takes place between original partners, disproportionation ought to occur as well. From the results given in Table I, a rough estimate of 0.02 can be obtained for the ratio of the rate of the disproportionation reaction [4] to the rate of the recombination reaction [2].† From this estimate and from the amount of ethylene formed in the lowest intensity runs (Table III), it follows that under these conditions less than 20% of the ethyl radicals recombine with propionyl radicals. In view of the fact that ethylene may also be formed in several other reactions, recombination between original partners may be considered negligible.

Recent work (15) on the liquid phase photolysis of mixtures of light and heavy acetone showed that deactivation is a more likely explanation for the low quantum yield than primary or secondary diffusive recombination. In earlier work (7) diacetone alcohol was determined in the liquid phase photolysis of undiluted acetone. It was also found that addition of hydrocarbons led to a decrease of the quantum yield of the volatile products (15) and the formation of an alcohol (6, 11). These results indicate that, besides dissociation and normal deactivation by collision, the following processes involving excited acetone molecules have to be considered:



When RH is a hydrocarbon like hexane or heptane, process *b* is faster than *a*. It may be mentioned that processes of type *b* have also been found to occur in the liquid phase photolysis of esters (1).

†In order to obtain this value the assumption was made that the CO quantum yield was one at 60° C., and a value of 0.12 was used for the ratio of the rate of reaction [12] to the rate of reaction [11].

The fact that at 28° C. addition of normal heptane to diethyl ketone increases the quantum yield of the volatile products to a value close to unity indicates that at these temperatures the process analogous to process *b* does not occur. A shorter lifetime of the excited diethyl ketone molecules may explain the difference in quantum yield between the liquid phase photolysis of acetone and diethyl ketone.

In analogy with the acetone photolysis, where a decrease of the quantum yield with temperature was found in both gas (14) and liquid (15) phase, it is quite possible that the low quantum yield at temperatures below 28° C. (Table II) is partly due to deactivating processes.

It has been suggested previously (5) that, in view of the relatively high ethylene yield, the following primary process occurs:



The fact, however, that the ethylene yield drops appreciably with intensity means that this compound is formed mainly in a radical-radical reaction. The iodine experiments (run 7) and the lowest intensity run of Table III indicate that the quantum yield of this process has to be lower than  $5 \times 10^{-3}$ .

#### *Secondary reactions*

Although their relative importance may change, the same secondary reactions can be expected to occur in both gas and liquid phase photolysis. In order to explain the liquid phase results, it has to be visualized that, owing to the higher ketone concentration, alkyl radicals will react mostly with diethyl ketone itself. Consequently, reactions of the ethyl radical with other radicals will be of less importance. Indeed, it can be seen from the data of Tables II and III that ethane is the main product. The fact that at higher temperatures the amount of CO formed is about half the amount of ethane proves that at these temperatures practically all of the propionyl radicals are decomposed.

As mentioned before, the decrease of the rate of formation of ethylene and butane with intensity points to the formation of these products in a radical-radical reaction. The data of Table II show that both compounds go through maxima around 28° C. This can be explained by a competition between an increase of the ethyl radical concentration caused by a substantial increase of the quantum yield up to 28° C. and the increase in rate of the hydrogen abstraction reaction [4] which tends to decrease the stationary radical concentration.

The  $\text{C}_2\text{H}_4/\text{C}_4\text{H}_{10}$  ratio is under all conditions considerably higher than the value of 0.12 generally accepted for  $k_{11}/k_{12}$ . Because no third body is required for processes [11] and [12] (8), the ratio for the two rate constants should be the same in both gas and liquid phase. It is probable that the excess ethylene is formed in a radical-radical reaction such as [4] and [14]. Reaction [4] may be expected to be of importance at low temperatures, while reaction [14] will occur mainly in the high temperature region.

If ethane and butane are produced only by reactions [10] and [11], the following relationship exists:

$$R_E/R_B^{1/2}[\text{K}] = k_{10}/k_{11}^{1/2} = A_{10}/A_{11}^{1/2}e^{-(E_{10}-\frac{1}{2}E_{11})/RT};$$

[K],  $R_E$ , and  $R_B$  represent respectively the concentration of diethyl ketone and the rates of formation of ethane and butane.

If this relation holds,  $R_E/R_B^{1/2}$  should be independent of the absorbed intensity.

The results given in Table III indicate that this ratio varies only slightly over a considerable intensity range. From this it may be concluded that ethane and butane are formed in normal kinetic processes.

In Fig. 1,  $\log R_E/R_B^{1/2}[K]$  calculated from the data of Table II has been plotted as a function of  $1/T$ . It can be seen that a good straight line is obtained which corresponds to an activation energy of 5 kcal./mole. This value may be ascribed to the activation difference  $E_{10} - \frac{1}{2}E_{11}$ . Gas phase studies in a temperature range from 25° to 150° C. lead to a value of 7.5 kcal./mole. The lower value obtained in the liquid phase photolysis may at least be partly due to the fact that, in a liquid, recombination of radicals may require an activation energy. In order to account for the difference between the gas and liquid phase photolysis results, a value of 5 kcal./mole has to be ascribed to the activation energy of the diffusion process.

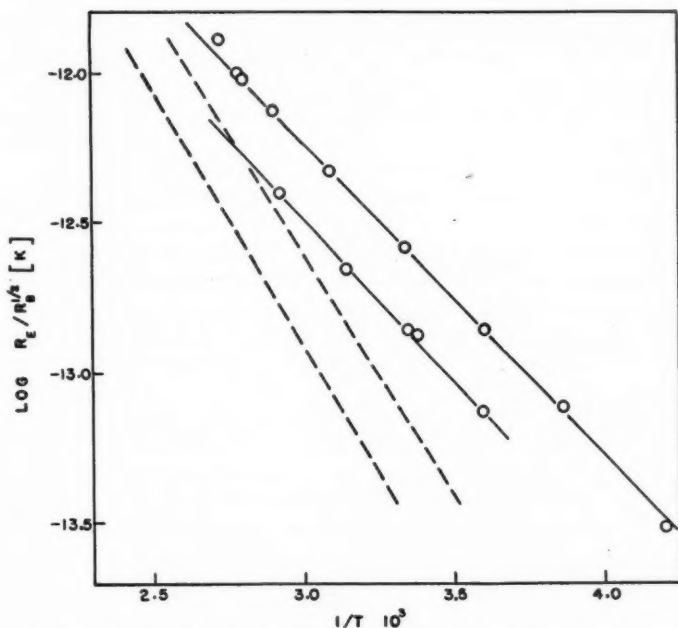


FIG. 1. Plot of  $\log R_E/R_B^{1/2}[K]$  against  $1/T$  for the photolysis of diethyl ketone and methyl ethyl ketone: ——— liquid phase photolysis: upper curve—diethyl ketone, lower curve—methyl ethyl ketone; - - - gas phase photolysis: upper curve—diethyl ketone, lower curve—methyl ethyl ketone.

In the above treatment, the ethane formed by reactions [3], [12], and [15] has not been taken into account. The low amount of butane formed shows reaction [12] to be unimportant. Assuming that reactions [14] and [15] on one side and [3] and [4] on the other side have comparable rates, it can be deduced from the low ethylene yield that the amount of ethane formed by reactions [3] and [15] is small compared to the amount formed by the abstraction reaction [10].

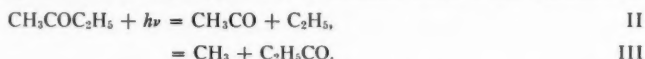
Addition of *n*-heptane and *n*-octane to diethyl ketone leads to a substantial decrease

of the ratio  $R_E/R_B^{1/2}$ . Increasing dilution apparently leads to a limiting constant value for this ratio which is about 22% of the one found for the undiluted diethyl ketone. These results point to an appreciably lower rate for the abstraction of a hydrogen atom from heptane and octane than from diethyl ketone itself. In agreement with this, a few gas phase photolysis experiments of equal diethyl ketone heptane mixtures at 95° C. (1) indicated that at least 80% of the ethyl radicals abstract a hydrogen atom from the diethyl ketone molecules.

#### *Methyl Ethyl Ketone*

##### *Primary Process*

Gas phase studies (17) have shown that two primary processes have to be considered:



At 3130 Å process II was found to occur about 10 times more often than process III.

The data given in Table V show that at higher temperatures, the methane and CO yields are approximately equal and appreciably lower than the ethane yields. From this it follows that in the liquid phase photolysis too, process II is the most important. The fact that at higher temperatures the ethane yield is approaching a constant value, which is approximately half that obtained in the liquid phase photolysis of diethyl ketone, indicates that in this temperature range the primary quantum yield is approximately the same for both compounds.

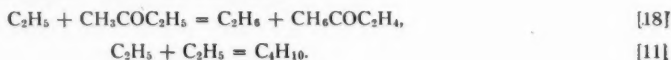
As in the liquid phase photolysis of diethyl ketone, the ethane yield increases slightly with decrease in intensity. From this it may be concluded that the low ethane yield at the lower temperatures is at least partly due to the disappearance of the ethyl radicals by normal radical recombination processes. However at low temperatures, diminishing intensities led to a decrease in the carbon monoxide and methane yields; this is contradictory to what was found in the liquid phase photolysis of diethyl ketone. It may be pointed out that liquid phase photolysis studies of several compounds where acetyl radicals are formed in the primary process led to the same observation (1). At high temperatures where normal thermal decomposition of acetyl radicals becomes important, an increase of the CO yield with decrease in intensity was found for all the compounds studied. Although no conclusive interpretation can be given, it is likely that at low temperatures CO and methane result from a radical-radical process.

The decrease in ethylene yield with diminishing intensity indicates that, as in the diethyl ketone photolysis, ethylene is produced mainly in a radical-radical process, instead of being formed in a primary process.

##### *Secondary Reactions*

Essentially the same reactions may be expected to occur as those described in an earlier paper on the gas phase photochemical decomposition of methyl ethyl ketone (4).

Only the following two reactions will be considered:



Then

$$R_E/R_B^{1/2}[K] = k_{18}/k_{11}^{1/2} = A_{18}/A_{11}^{1/2}e^{-(E_{18}-\frac{1}{2}E_{11})/RT}.$$

The data of Table V indicate that the ratio  $R_E/R_B^{1/2}$  is practically independent of intensity, which substantiates the above relationship.



In Fig. 1,  $\log R_E/R_B^{1/2}[K]$  has been plotted against  $1/T$ . It can be seen that this Arrhenius curve corresponds to an activation energy which is about the same as the one found for diethyl ketone. The two plots are separated by approximately 0.3 logarithmic units. The dashed lines which represent the gas phase results for the hydrogen abstraction reaction from diethyl ketone (3) and methyl ethyl ketone (4) show clearly that these plots are also approximately parallel and show the same separation as the liquid phase Arrhenius curves. These results can be explained by assuming that mainly secondary hydrogen atoms are abstracted from the ketones.

As mentioned earlier, the lower values found for the activation energy differences  $E_{12} - \frac{1}{2}E_{11}$  and  $E_{13} - \frac{1}{2}E_{11}$  in the liquid phase experiments may be due to the fact that diffusion of radicals in a liquid requires an activation energy. However, solvation of the reactants and activated complexes may also influence the rate of the abstraction and recombination reactions.

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**THE HEMICELLULOSE OF WHITE ELM (*ULMUS AMERICANA*)**  
**I. IDENTIFICATION OF 2-O-(4-O-METHYL-D-GLUCOPYRANOSYLURONIC ACID)-**  
**D-XYLOPYRANOSE<sup>1</sup>**

J. K. GILLHAM AND T. E. TIMELL

ABSTRACT

Alkaline extraction of wood meal from white elm (*Ulmus americana*) has yielded a hemicellulose which on hydrolysis gave a sugar mixture containing xylose together with traces of galactose, glucose, mannose, and rhamnose in addition to two monouronic acids and one aldobiouronic acid. The latter was identified as 2-O-(4-O-methyl-D-glucopyranosyluronic acid)-D-xylopyranose.

This series of investigations deals with the constitution and properties of the hemicellulose portion of white elm wood. The present paper is concerned with the structure of an aldobiouronic acid obtained on partial hydrolysis of the latter.

RESULTS AND DISCUSSION

Alkaline extraction of wood meal from white elm gave a hemicellulose in a yield of 16.5%, or slightly higher than the methyl glucurono-xylan content of the wood, 15.4% (1). Hydrolysis of the crude hemicellulose yielded a sugar mixture containing six sugar acids and xylose as well as traces of galactose, glucose, mannose, and rhamnose. The acids were separated from the neutral sugars by the use of an anion exchange resin and were then resolved on a column containing the same resin by eluting with dilute acetic acid. Three main fractions were obtained, corresponding on the paper chromatogram to an aldobiouronic acid, a monouronic acid, and a methyl monouronic acid, respectively.

The methoxyl content and the equivalent weight of the aldobiouronic acid as well as chromatographic evidence suggested that it was a methoxyuronic acid linked to a pentose. A portion of the acid was converted to the methyl ester methyl glycoside, reduced with lithium aluminum hydride, and hydrolyzed. Examination on the paper chromatogram indicated the presence of 4-O-methyl-D-glucose and D-xylose; the latter crystallized and the former was identified through its crystalline osazone (2, 3).

The aldobiouronic acid was completely methylated and the methyl ester methyl glycoside was reduced and hydrolyzed. The two methylated sugars obtained were separated and identified through their crystalline aniline derivatives as 3,4-di-O-methyl-D-xylose and 2,3,4-tri-O-methyl-D-glucose, respectively (4, 5). The methylated aldobiouronic acid was accordingly methyl 2-O-(2,3,4-tri-O-methyl-D-glucopyranosyluronic acid)-3,4-di-O-methyl-D-xylopyranoside methyl ester. This conclusion was further corroborated by the fact that it gave the same infrared spectrum as a compound with this structure, previously isolated from white birch wood (6). The aldobiouronic acid was therefore 2-O-(4-O-methyl-D-glucopyranosyluronic acid)-D-xylopyranose. Confirmation of this structure was obtained from lead tetraacetate oxidation, which produced 1.2 moles of formaldehyde per mole of acid (7), a result to be expected only from a 1,2-linked disaccharide (8, 9).

The synthesis of one or both of the existing anomers of this compound is presently being attempted (10) to determine the nature of the glycosidic linkage. The high positive rotation of the compound (+110°) as well as earlier evidence (11) indicate that it is probably of the  $\alpha$ -type.

<sup>1</sup>Manuscript received October 31, 1957.

Contribution from McGill University and Pulp and Paper Research Institute of Canada, Montreal, Quebec.

The aldobiouronic acid isolated here is identical with that obtained on partial hydrolysis of a number of other hardwood hemicelluloses, including those from trembling aspen (12), American beech (13), European beech (14), and white birch (6). It has also been tentatively identified in the hydrolyzate of hemicelluloses from Finnish birch (15), yellow birch (16), and *Eucalyptus regnans* (17).

#### EXPERIMENTAL

All specific rotations are equilibrium values and melting points are corrected. Evaporations were carried out *in vacuo* at 40° C.

##### *Paper Chromatography*

Solvents used for separating the sugars were (A) ethyl acetate:acetic acid:water (9:2:2), (B) 1-butanol:pyridine:water (10:3:3), and (C) 1-butanol:ethanol:water (40:11:19). Separations were carried out on Whatman No. 1 filter paper by the descending technique. The spray reagent was *o*-aminodiphenyl (18).

##### *Isolation of the Hemicellulose*

Extractive-free white elm wood meal (500 g., 40–60 mesh) was extracted in a nitrogen atmosphere with 4 liters of 24% (w/w) aqueous potassium hydroxide by shaking for 2 hours at room temperature. The extract was separated from the alpha-cellulose by filtration through sintered glass and was poured slowly with stirring into a mixture of glacial acetic acid (1.5 liter) and anhydrous ethanol (12 liters), cooled to -16° C. The precipitated hemicellulose was collected on a centrifuge at -20° C., was washed five times each in succession with 80% aqueous ethanol, anhydrous ethanol, and petroleum ether (b.p. 30–60° C.), and was finally dried *in vacuo* at room temperature over calcium chloride for 1 week. The yield was 82.5 g., corresponding to 16.5% of the original wood.

Acid hydrolysis and subsequent examination by paper chromatography (solvents A and B) indicated the presence of six sugar acids and xylose in addition to traces of galactose, glucose, mannose, and rhamnose.

##### *Separation of Sugar Acids*

Hemicellulose (75 g.) was partially hydrolyzed with sulphuric acid (19). After neutralization with barium carbonate and filtration through Celite, the sugar acids were adsorbed on a column of Dowex 1-4X anion exchange resin (carbonate form). Neutral sugars were removed by washing with water, after which the sugar acids were eluted with *N* sulphuric acid. The latter was removed with barium carbonate, barium ions were eliminated by treatment with Amberlite IR 120 exchange resin, and the solution was concentrated to a sirup (10 g.).

A portion of the material (7 g.) was added to the top of a column (160×5 cm.) containing Dowex 1-4X exchange resin (acetate form) and the sugar mixture was resolved by eluting with *N* acetic acid. Analysis of the fractions collected (18) indicated the presence of six sugar acids, one of which (2.5 g.) was chromatographically identical with an aldobiouronic acid previously obtained from white birch wood (6). Two others corresponded in position and color reactions to galacturonic or glucuronic acid (5–10 mg.) and 4-*O*-methyl-D-glucuronic acid (500 mg.). Anal. Calc. for  $C_{12}H_{20}O_{11}$  (aldobiouronic acid):  $OCH_3$ , 9.1%; equiv. wt., 340. Found:  $OCH_3$ , 8.8%; equiv. wt. 369.  $[\alpha]_D^{20} +110^\circ$  (*c*, 2.2 in water).

##### *Reduction and Hydrolysis of the Aldobiouronic Acid*

The aldobiouronic acid (975 mg.) was converted to its methyl ester methyl glycoside by refluxing with 2% methanolic hydrogen chloride (50 ml.) for 8 hours. Neutralization

with silver carbonate and evaporation yielded a sirup which was dissolved in tetrahydrofuran (50 ml.) and reduced with a solution of lithium aluminum hydride (1.2 g.) in 75 ml. of the same solvent (20). Hydrolysis of the neutral disaccharide with *N* sulphuric acid, neutralization with barium carbonate, and concentration yielded a sirup which showed two spots of equal intensity on the paper chromatogram with solvent B, corresponding in color reaction and position to xylose and 4-*O*-methyl-D-glucose.

#### *Identification of Hydrolysis Products*

The sugar mixture was added to the top of a column (1.5×15 cm.) containing coconut charcoal. Elution with 2% and 10% aqueous ethanol yielded D-xylose (322 mg.) and 4-*O*-methyl-D-glucose (395 mg.), respectively. The xylose crystallized and had m.p. and mixed m.p. 144.5° C.,  $[\alpha]_D^{20} +18^\circ$  (*c*, 3.2 in water). The 4-*O*-methyl-D-glucose was converted to its osazone derivative (2), m.p. and mixed m.p. 157° C. It was distinguished from 4-*O*-methyl-D-mannose by treatment with hydrogen bromide (21), after which glucose was the only sugar detectable on the paper chromatogram. Anal. Calc. for  $C_7H_{14}O_6$ :  $OCH_3$ , 16.0%. Found:  $OCH_3$ , 15.8%.

#### *Methylation of the Aldobiouronic Acid*

The aldobiouronic acid (826 mg.) was dissolved in water (10 ml.), dimethyl sulphate (10 ml.) was added, and then dropwise over a 12-hour period 30% (w/w) aqueous sodium hydroxide (30 ml.). Two further methylations were carried out with powdered sodium hydroxide (18 g.) and dimethyl sulphate (25 ml.). The material was recovered in the usual way by extraction with chloroform and was then methylated four times with methyl iodide (20 ml.) and silver oxide (6 g.) to yield a clear sirup (439 mg.). The infrared spectrum of the latter indicated the absence of any free hydroxyl groups and was identical with the spectrum of methyl 2-*O*-(2,3,4-tri-*O*-methyl-D-glucopyranosyluronic acid)-3,4-di-*O*-methyl-D-xylopyranose, previously obtained from white birch wood (6).

#### *Reduction and Hydrolysis of the Methylated Aldobiouronic Acid*

The sirup was dissolved in anhydrous ether and reduced with lithium aluminum hydride in the same solvent. The reduced material was subjected to methanolysis and was then hydrolyzed with 0.5 *N* hydrochloric acid (25 ml.) for 10 hours. The acid was removed with silver carbonate and the solution was deionized with Amberlite IR 120 and Dowex 1-4X (acetate form) exchange resins. Examination by paper chromatography revealed the presence of two components, corresponding to 2,3,4-tri-*O*-methyl-D-glucose and 3,4-di-*O*-methyl-D-xylose.

#### *Identification of 2,3,4-Tri-*O*-methyl-D-glucose and 3,4-Di-*O*-methyl-D-xylose*

The sugar mixture was resolved on a charcoal column (1.5×15 cm.) by eluting with 20% aqueous ethanol to yield chromatographically pure sirups of a tri-*O*-methyl glucose (180 mg.) and a di-*O*-methyl xylose (169 mg.). Anal. Calc. for  $C_9H_{18}O_6$ :  $OCH_3$ , 41.9%. Found:  $OCH_3$ , 41.5%.  $[\alpha]_D^{20} +78^\circ$  (*c*, 3.5 in water). The tri-*O*-methyl glucose was converted to the aniline derivative, 2,3,4-tri-*O*-methyl-*N*-phenyl-D-glucosylamine, m.p. 144° C. Anal. Calc. for  $C_{17}H_{24}O_5$ :  $OCH_3$ , 34.8%. Found:  $OCH_3$ , 34.3%.  $[\alpha]_D^{20} +20.3^\circ$  (*c*, 2.2 in water). The 3,4-di-*O*-methyl-*N*-phenyl-D-xylosylamine had m.p. 115–116.5° C. after recrystallization from ethyl acetate.

#### *Oxidation of the Aldobiouronic Acid with Lead Tetraacetate*

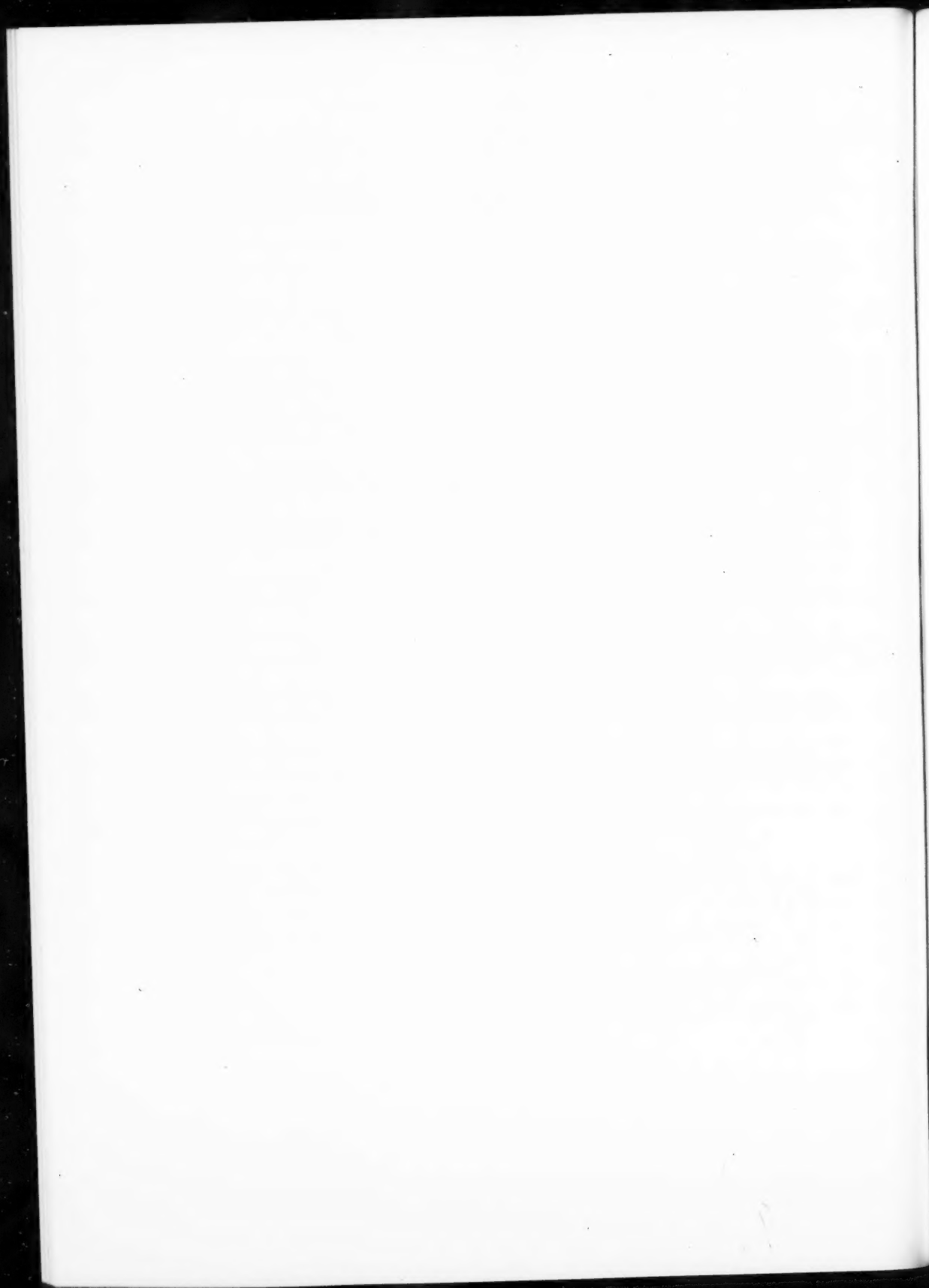
The oxidation of the aldobiouronic acid was carried out by the method of Perlin (7, 8) in the presence of potassium acetate. The formaldehyde was determined by the dimedon method, the crystalline precipitate having a m.p. of 188.5° C. (22).

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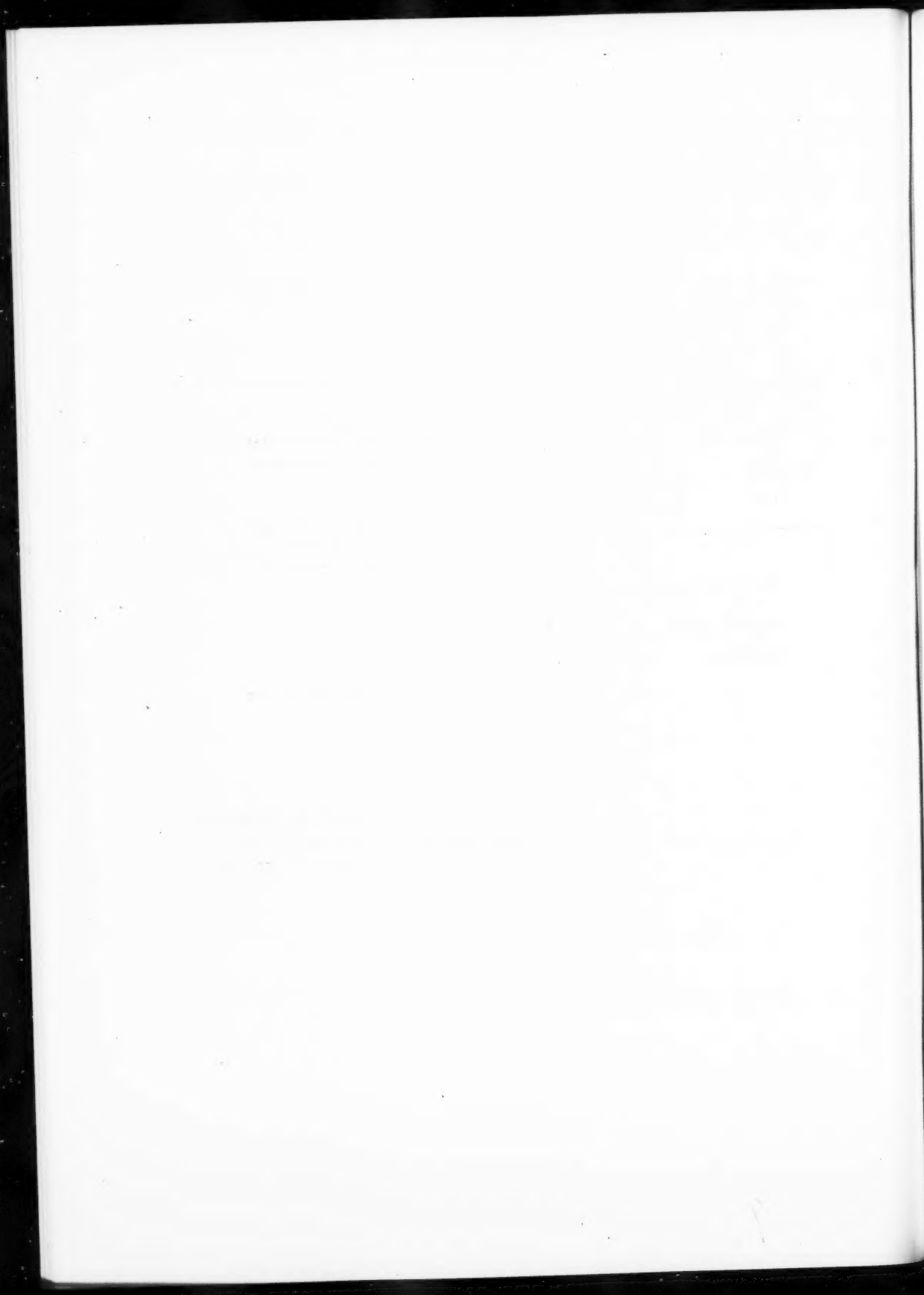
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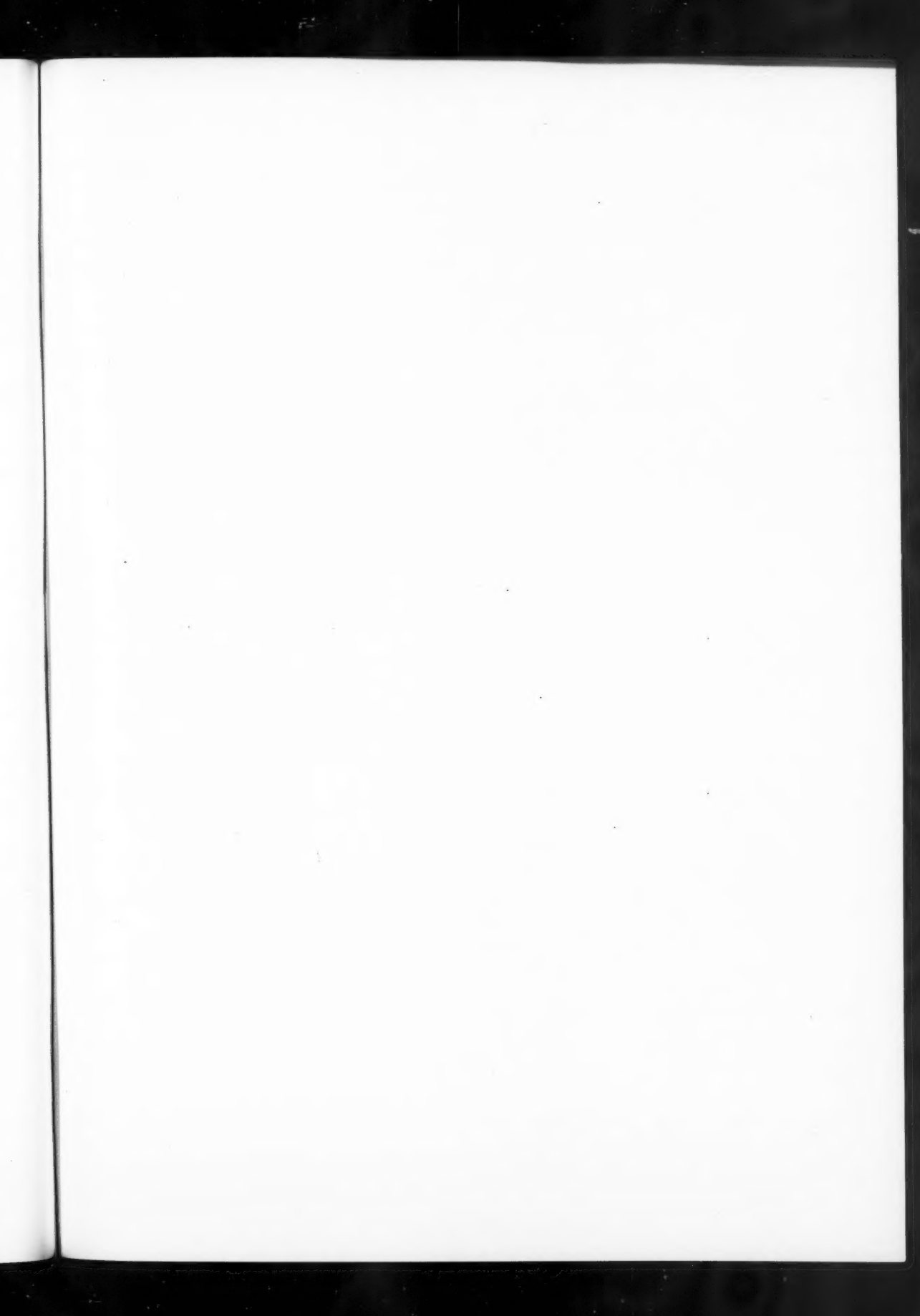
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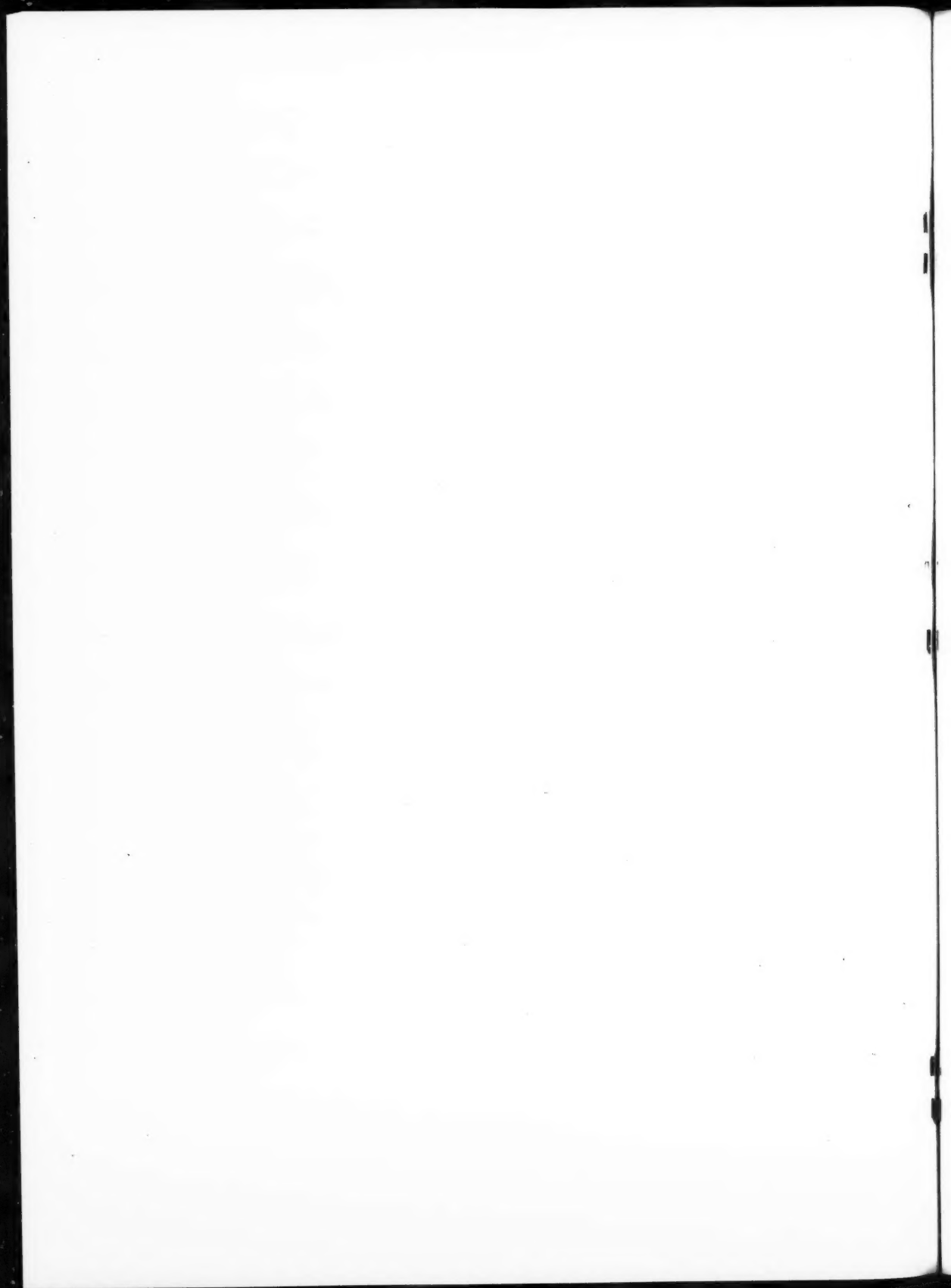
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